THE REACTIONS OF COAL IN A HIGH INTENSITY ELECTRIC ARC

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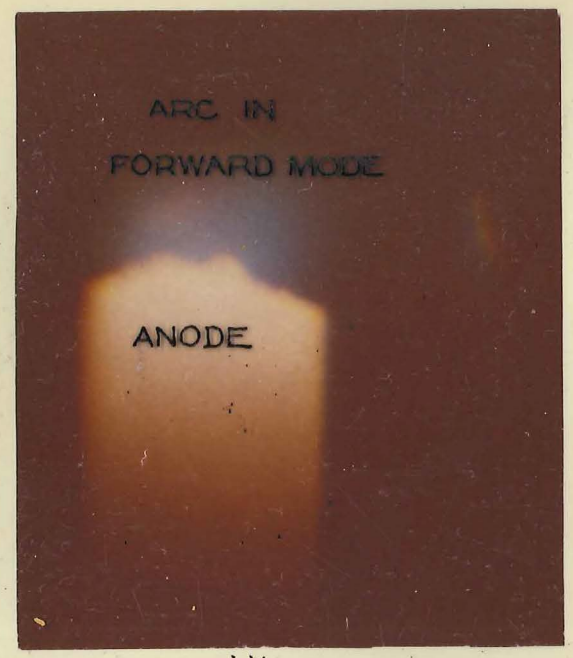
H_2 FLOW THROUGH EACH CATHODE $0.7\ g\ h^{-1}$



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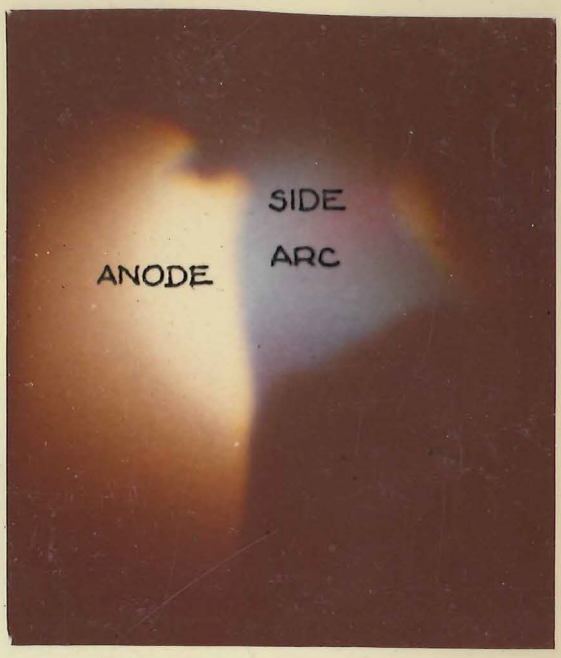

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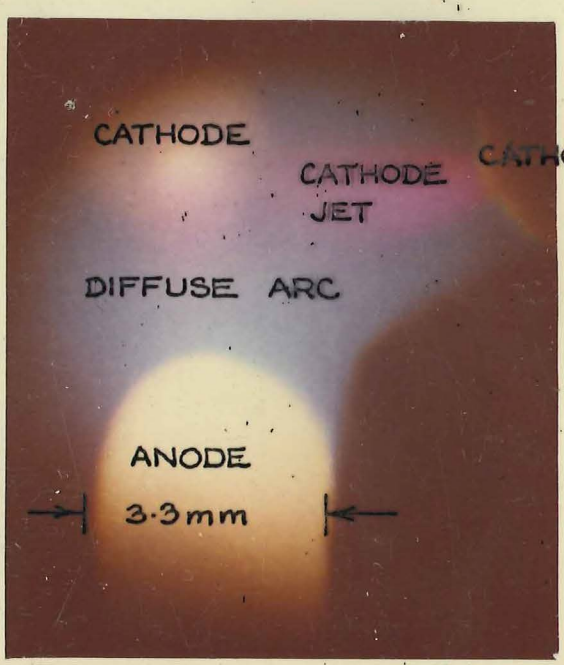

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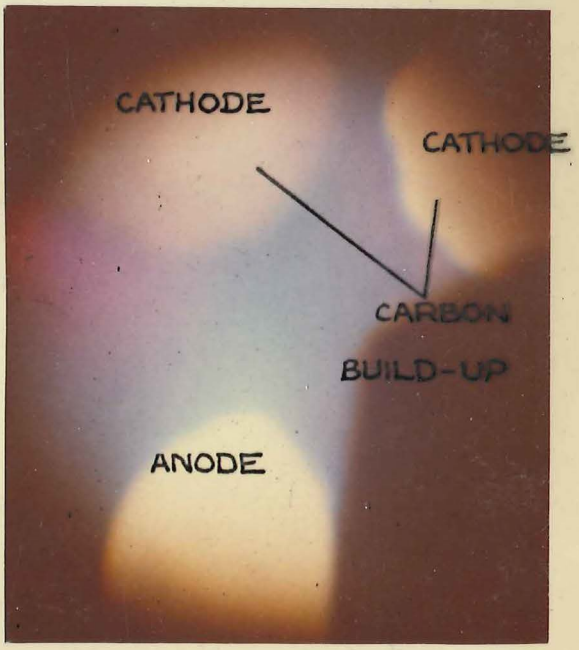

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FRONTISPIECE — LOW AND HIGH CURRENT CARBON ARC OPERATION IN HYDROGEN

ABSTRACT

The aim of the project reported here was to develop an efficient means of converting coal to acetylene, with a view to using the acetylene for a New Zealand-based plastics industry. When the project was begun in 1967 coal was the only feasible indigenous raw material. An economic survey was carried out on the manufacture of acetylene and its competitor ethylene in well industrialised countries in order to determine suitable economic criteria. A more intensive study was made of the possibilities of Polyvinylchloride manufacture in New Zealand, using ethylene from imported naphtha or acetylene from coal and lime via the carbide process.

Following the success of certain electric arc devices in making acetylene from gaseous and liquid hydrocarbons, but noting the failure of the same devices with a coal feed, a different electric arc reactor was designed specifically for use with coal. The basis for the design was the "high intensity carbon arc", which is commonly used as a light source in searchlights etc. When the current density on the positive carbon electrode of such arcs is high, rapid evaporation of the carbon occurs. Anodes for such a reactor were envisaged to be made from coal, but for convenience in this experimental study were graphite rods.

A small reactor designed for a maximum current of 100A and a mass throughput of carbon and hydrogen of a little over 100 g h^{-1} was built and operated at currents up to 50A and throughputs of about 70 g h^{-1}. Graphite rods of 3.3 mm diameter

were ablated in an atmosphere of hydrogen. Successful configurations were evolved for both the insulating surround of the anode and the cathode tips, where hydrogen flows were used to irrigate the surfaces and insulating gaps to ensure continuous operation. Rapid cooling of the hot mass flow from the reactor was necessary, and this was achieved simply by passing the flow through a water-cooled tube. Measurements were made of all energy flows and all mass flows so that balances over the apparatus could be attempted. Measurements were also made on the light emitted by the anode and arc by a spectrograph and thermopile. Coloured photographs were also taken. Electron-micrographs were made of the soot from the reactor.

A maximum of about 65% conversion of carbon to carbon in acetylene was obtained, and under another set of conditions the highest acetylene concentration of 11.8% was obtained in the off-gases. The minimum energy requirement was 130 kwh $(\text{kg acetylene})^{-1}$. Under the one set of conditions a conversion of 55% was obtained with a concentration of 8 mol % and an energy requirement of 130 kwh kg^{-1}. These values can be compared with economic criteria of 30% conversion, 8 mol % and 11 kwh kg^{-1}. Soot formation was small.

An enthalpy-composition chart was made for the carbon-hydrogen system for temperatures from 2000 to 6000K, and a pressure of 1 bar, using 23 molecular and atomic species. It was found that the experimental results could be predicted using the thermodynamic calculations by the hypothesis that the gas mixture supercools with respect to soot ("graphite"), that gas phase

equilibrium is attained before quenching, and that species other than free radicles are preserved during the quench. This hypothesis also accounts for the results of plasmatron studies with methane. Another hypothesis was proposed to account for the continuous radiation observed, and the consistent unexplained loss of carbon from the reactor. It was proposed that solid graphite fragments came off the anode with the carbon molecules previously assumed, and that these fragments existed in the arc. Some consequences of this hypothesis with respect to the functioning of the arc were outlined.

Using both these theories, together with observations made on the present reactor and an energy flow analysis of the anode, predictions were made on the performance of larger reactors for acetylene manufacture. Acetylene concentrations up to 55 mol % were predicted. It was predicted that closer control of the enthalpy of the hydrocarbon mixture before quenching could raise the concentration from the observed 10 to 12 mol % to 25 to 30 mol % for the same conditions otherwise. An increase in size was predicted to reduce the energy consumption by an order of magnitude. It was predicted that the reactor could be operated economically in two ways - firstly by using predominantly natural gas as a feed, and a coal/anode carbon feed only to increase the concentration above that possible with natural gas, and secondly to use predominantly coal, with perhaps some natural gas. In both cases the predicted energy requirements were below that for the plasmatron operating with natural gas. It was concluded that further development towards larger reactors was worthwhile, to test these predictions.

INTRODUCTION

CHAPTER 1

1.1 Economic Impetus

New Zealand has an abundance of coal in relation to its population, and is able to make electric power cheaply. These two economic facts taken together may give the answer to a two-sided problem in foreign exchange. On the one hand, New Zealand may be presently spending over 10 million dollars per year on polyvinylchloride imports (Appendix 1), but on the other hand may export coal to Japan on a scale which is significant compared to New Zealand's reserves.

The major market for coal in the world is the fuel market, where it is in competition with petroleum and natural gas. However, as the oil producing states realise that their reserves are not unlimited and become more politically aware of the share of profits they can claim, the price of petroleum will rise, placing more importance on coal, for which there is an estimated world reserve of about twenty times that of oil, and more importance on natural gas, for which the estimated reserve is about that of oil. An increasing part of the oil and gas used is being converted to useful chemicals via ethylene and benzene, whereas after an initial good start in the 1940's, the chemicals industry based on coal is suffering a decline. Reasons for the differing fortunes of the different industries are the ease of handling oil and natural gas compared to coal, the comparative cheapness (up to the present) of oil and natural gas condensates, and the comparative ease of developing efficient techniques for

the chemical conversions required with petroleum and natural gas fractions. Suitable petroleum fractions and natural gas condensates merely require the breaking of a few carbon-hydrogen bonds to create a mildly reactive intermediate, ethylene (or another olefin), which is used for the manufacture of plastics and other materials. Coal, on the other hand, requires no less than a complete rearrangement of atoms in order to form a similar hydrocarbon intermediate, and the high temperatures necessary for the tearing-apart process favour acetylene as a product which is more reactive than ethylene.

It was seen at the start of this project that the dissipation of electrical power was the most likely means of reaching the temperatures necessary for the rearrangement of coal, and so the development of technology for this purpose seemed particularly appropriate for New Zealand. Various devices existed for the production of acetylene from methane, which needs a similarly severe treatment for conversion to a two-carbon-atom intermediate, as each molecule of methane has only a single carbon atom. The reaction of coal had also been attempted in these devices. However, owing to the particulate nature of coal, only very limited reaction was achieved. There was a need for a device designed specifically for a solid feed, allowing for the properties of carbon bearing materials at higher temperatures, especially those derived from coal. If such a device could be developed to produce acetylene economically from coal, the domestic manufacture of plastics such as P.V.C. is likely to become more attractive, and attention may also be directed to the potential value of

New Zealand's coal reserves, with more thought given to their disposal.

In the long term, in industrialized countries with pollution problems, another reason for developing a chemical reactor for a solid carbon bearing feed can be seen. Many wastes contain a high proportion of both hydrogen and carbon paper, sewage and plastics being examples. The carbon matter in many wastes is difficult to dispose of except by burning, which also causes pollution. If such wastes could be treated to become suitable feed to be converted to acetylene, a mass recycle could be achieved, requiring electrical energy to convert waste materials to building materials.

Since this project was begun, significant finds of condensate-free natural gas have been made in New Zealand. It may appear that the purpose for the development of a coal-electric power reactor has disappeared on the New Zealand scene, in view of the possibility of using plant (plasmatron) already developed overseas for the reaction of methane. The use of methane with a plasmatron appears to impose a definite upper limit on the acetylene concentration (20 mol %) and a lower limit on the energy requirement (9 kwh (kg acetylene)$^{-1}$. While these values appear economically attractive in New Zealand, it is shown in this thesis that there is a good possibility that the concentration could be raised, and the energy requirement dropped by the use of both coal and methane, or coal by itself.

To provide some reference by which to gauge the economic potential of a new process, an economic study was made of the

possibility of polyvinylchloride manufacture in New Zealand using well established processes. The reader is referred to Appendix 1 for an account of this.

1.2 Arc Physics

The electric arc was chosen as the mechanism by which electrical energy was to be dissipated, because of the associated ease of reaching high temperatures, the relatively high efficiency in the use of the energy, and the rapidity of heating. The reader will be given below a brief discussion of the properties of arcs, as far as they are known, and in particular the properties of the arc with a carbon anode, as this is the arc used in this study. Many excellent texts exist on gaseous discharges. A classical work is that of J.J.Thompson and his son, G.P.Thompson, published in 1903 and in 1932, but still useful today (1). A more recent treatment has been given by J.D.Cobine (2), who concentrated on the industrial uses of gaseous discharges. A number of comprehensive articles have appeared from German physicists (3, 4 for example), describing measurements and theory of arcs. The most useful discussion in this author's opinion to help in understanding the properties of arcs is contained in a book by Hoyaux (5), which deals with the many theories of arcs in a critical manner with a view to estimating arc properties in engineering situations.

The general texts on electric discharges devote only a handful of pages to the high pressure arc, and the reason for this is apparent. There are very few straightforward measurements

which have been made on these arcs, because the high temperatures either prohibit the introduction of measuring instruments, or make necessary a large energy transfer from the arc, thus perturbing it severely in the 'measured' area. Overall electrical measurements can be made unambiguously, and some measurements can be made on the electromagnetic radiation associated with an arc. Yet even with optical spectroscopy, elaborate checks must be made on the assumptions used to interpret the radiation intensities, before one has confidence in, say, a temperature measurement. Only very recently has the data necessary for such work become available, and then only for a few chemical systems.

An arc can be defined as a gaseous discharge with a low voltage (order of tens of volts) and a current greater than 0.1 to 1 A. Arcs can be divided into low and high pressure arcs, with the high pressure arc the type usually referred to as an "arc". The gas forming an arc consists of a collection of electrons, positive ions and molecules, the charged species acquiring drift velocities under a weak electric field. Since electrons have a much smaller mass than the positive ions, but normally the same charge, they gain kinetic energy from the electric field much more rapidly than the positive ions, and incidentally carry much more of the total current. The distribution of this electron energy to the other species depends on the gas pressure. The exchange of energy by collision from an electron to a much larger neutral molecule is very inefficient because of the difference in mass, and many collisions are needed before all species have similar kinetic energies.

Thus with low pressure arcs ($< 10^{-2}$ bar) where collisions are few, electron temperatures of the order of thousands of Kelvins are estimated from the kinetic energy distributions, whereas the "gas" temperature, which can be measured with a thermometer, does not rise much above room temperature. With high pressure arcs ($> 10^{-1}$ bar) collisions are frequent, and it is generally held that the electron temperature does not rise above the "gas" temperature by more than a few percent. Temperatures from 8000 to 12000K are commonly measured by spectroscopic means, for arcs at a pressure of 1 bar.

Electrical neutrality is closely maintained down to a very fine scale in high pressure arcs ($\sim \mu$m), except where the arc joins the cathode or anode. Superimposed on this neutrality in any small volume in the arc is a very slight non-neutrality from one part of the arc to the other, as required by the operating electric field of the arc. Arguments such as those just mentioned have prompted writers to divide the high pressure arc into three distinct regions, each of which is usually considered independent from the others. The arc column, with a low voltage gradient is distinguished from two small regions at either end of it, the cathode fall region and the anode fall region, each with high voltage gradients. Some estimates of the voltage gradient in the arc column have been made from measurements of arc voltage with rapidly changing length. These estimates range from $0.5 v\ mm^{-1}$ for a mercury arc to $9 v\ mm^{-1}$ for an arc in hydrogen, both at a pressure of 1 bar and a current of 10 A (2). The values of the voltage drop across the cathode fall or anode

fall, to this author's knowledge, have not been measured unambiguously for any high pressure arcs.

Most arcs have a voltage which decreases with increase in current, and this is reflected also in the dependence of the measured voltage gradients on current. Thus the change in voltage has been identified with a change in properties of the arc column, and the interpretation is that the diminished importance of heat transfer from the arc at high currents (and larger size) allows higher temperatures, greater ionization and appreciably lower overall arc resistance. However, certain arcs, those where no further reduction in arc resistance is possible, do have rising voltage characteristics. An arc forced to operate through a cool constriction at a high current is one example, and an arc operated with carbon electrodes at a high current is another.

The most significant characteristic about the arc for many purposes is that it is self-sustaining. The emission of sufficient electrons from the cathode is the first necessary feature of arc operation, and these are emitted from the cathode surface under the thermal or electrical interaction with the arc. The cathode mechanism has not been satisfactorily resolved.

1.3 The Carbon Arc

The arc struck between two carbon or graphite rods behaves similarly to other arcs of the same current and pressure for low currents. Mason (6) found a voltage gradient of about

3v mm^{-1} by a probe method for such a vertical arc of about 10 A current.

At higher currents the anode of a carbon arc begins to erode rapidly, showing an incandescent plume directed away from the anode. For anodes of 3 to 10 mm diameter, current densities on the anode above about 100 A cm^2 are associated with rapid removal of carbon. According to Finkelnburg, who worked with 'hard' and 'soft' carbons baked to 1500K, close study of the anode attachment of the arc revealed that a strong contraction occurs with the hard core carbons in air once the current density exceeded 40 A cm^{-2} on the anode. As the current is increased, this contraction occurs simultaneously with a sudden drop in arc voltage, and the start of a hissing noise. The soft core carbons Finkelnburg used (see Chapter 8 for a description of the carbons) showed the hissing phenomenon only over a certain range of currents, the arc becoming quiet again for higher currents. Carbons which were loaded with a high fraction (40 mass %) of metal salts ("Beck carbons") did not show the hissing behaviour, but instead, formed a deep crater over which the steady arc was distributed.

The voltage of both the hissing and non hissing high current carbon arc was found by Finkelnburg to rise with current. Finkelnburg proposed that this higher current arc with the rising voltage characteristic be called the "high intensity carbon arc", to distinguish it from the lower current arc with the falling voltage characteristic which he called the "low intensity carbon arc". It is the "high intensity" carbon arc which was used in this project, and which has been widely used as a light source.

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RECENT ATTEMPTS AT COMMERCIAL PRODUCTION OF ACETYLENE

CHAPTER 2

Contents

Economic background. partial oxidation of methane. indirect pyrolysis of hydrocarbons and coal. glow discharge with methane and coal.

Arc discharge methods (1) gas feeds - Hüls plant. plasmatrons. simple chemistry. rotating arc devices.

(2) coal feeds - plasmatrons. AVCO coal reactor.

Comparison of methods - energy use. yields. concentration.

Optimisation - scale. pressure. mixing. reaction time.

2-A Introduction

All acetylene manufacturing methods except the carbide process achieve a direct combination to acetylene of the elements hydrogen and carbon present in molecular fragments at high temperatures. The methods consist of two steps. Vigorous heating of the feed to break down large molecules to suitably small fragments, is followed by rapid cooling, to preserve the acetylene formed. Both steps must be rapid, and their velocity is dictated by the velocity of the reaction to solid carbon and gaseous hydrogen, which can occur in both steps. In practice, a minimum temperature for good acetylene yield is found with each feed. This minimum varies from about 1500K to 1800K.

Economic criteria are

(1) energy consumption for a given mass of acetylene

(2) the fraction of the feed converted to acetylene

(3) concentration of acetylene in the off-gas.

2-B Partial Oxidation of Hydrocarbons

B1 Recent economics

Since 1940, several polymers have been made from acetylene available from the carbide process. From 1950, this situation was challenged strongly by the use of ethylene available from the pyrolysis of petroleum fractions and natural gas condensates (1) (Appendix D). In an attempt to reverse this trend, those organisations committed to acetylene technology developed methods of producing acetylene from methane in natural gas, and from naphtha, a petroleum fraction. The idea which received most attention was the oxidation of some of the feed so that the remainder was heated sufficiently for acetylene to form. After this "partial oxidation", the hot gases were cooled quickly to prevent decomposition of acetylene.

Several partial oxidation processes were made commercial. The more successful produced acetylene for about 13-18 c kg^{-1} compared with 29-30 c kg^{-1} for the carbide process (Appendix D). This economy still did not compete fully with the low costs of ethylene, which are down to 5 c kg^{-1} for very large plants. The partial oxidation acetylene plants are thus used only where there are favourable circumstances, such as the presence of cheap natural gas with no condensate.

B2 Industrial Plant

During the 1950's, B.A.S.F. (Badische Analin and Soda-Fabrik, Germany) developed a premixed flame reactor with a water quench for use with feeds of methane and oxygen. Typical conversions to acetylene were 30% by mass of methane, with

concentrations of 8 mol % in the product gas. Purification costs were heavy because of the low concentration. Limitations were imposed (2) on the scale of this reactor by the need for control of velocities over the whole cross section of flow, and by the need for a rapid quench for all the gas.

Larger reactors were built which used the hot gases from combustion of a gaseous hydrocarbon (typically methane) to mix with and pyrolyse a liquid hydrocarbon (typically naphtha). Reactors which used this idea were developed by SBA-Kellogg (Soolte Belde Asot, Netherlands), Montecatini (Italy) and Hoechst (Germany). Ethylene as well as acetylene was produced from the heavy feed, in a combined yield of 45 to 65 % by mass of the total feed. These two stage reactors were more commercially attractive on the industrial scale than the single stage reactor. Steam was introduced into the reactor in order to reduce coking and to improve the yield. The success of this tactic may be attributed to the diluting effect of steam on the acetylene decomposition reaction, which is second order. Typical pyrolysis times with these reactors were 1-5 ms.

B3 Pilot Plant

The development of a partial oxidation reactor for a single natural gas feed with greater throughput than the BASF type has engaged many Russian workers (2). Some success was achieved by designs to promote greater turbulence in the flame. The difficulties of soot formation and coking experienced with feeds of high carbon to hydrogen ratio have been relieved by two novel designs. A submerged flame reactor developed by BASF (3) has

allowed the use of crude petroleum as a raw material, as do various fluidised bed techniques (4) which burn off deposited carbon on the carrier particles in a separate chamber.

2-C Indirect Pyrolysis of Hydrocarbons and Coal

C1 Vapour feeds

The pyrolysis of hydrocarbons for acetylene production by heat transfer from a hot wall has been industrially proven in one process. The Wulff process heats a fixed bed of large thermal capacity by burning a cheap fuel through it, and subsequently passes through a hydrocarbon. There have been reports about Wulff plants of sooting problems so severe that permanent shut down was considered. However favourable economics are quoted as late as 1967 (2) (12 c kg^{-1} acetylene) and new plants have been reported.

Othmer, Happel and Kramer (5, 6) have achieved over 96% conversion of methane to acetylene with pyrolysis in electrically heated alumina tubes, at temperatures up to 2100K. Typical product compositions were, in mol %; acetylene 21%, hydrogen 74%, methane 5%, with a small amount of soot. The absolute operating pressure used was 0.13 bar. The authors claim capital costs from 11 to 18 U.S.c. per annual production of 1 kg, and so claim production costs from 7 to 11 U.S.c. kg^{-1} acetylene in favourable locations in the United States. An industrial plant was planned in 1965, but the process has not been mentioned since in the literature.

C2 Coal feed

Kröger and Rao (7) heated pulverised coal in the size range 80-180 μm for about 0.2 to 1 s, by passage through tubes at

temperatures from 1200-1900K. A yield of acetylene of 8% by mass of coal was obtained at 1900K from a coal with high volatile content. From the mass of coal used, 50% or more was found as a char with very little volatile content, 25% was found as gas, and 15% as soot. The product gas contained 12 mol % acetylene, 70 mol % hydrogen, and 18 mol % carbon monoxide. The atomic C/H ratio of the gases driven from the coal, including the soot formed from the gas phase, was 0.54, compared with that in the coal, of 1.28.

Pichler (8) passed pulverised coal through a heated alumina tube at temperatures up to 1970K, and investigated the effect of tube temperature, coal particle size, pressure, hydrogen carrier gas flow rate and the type of coal, on the quantity of acetylene obtained. He found that the yield increased with increase in temperature from 1600 to 1970K, and was a maximum for a particle size of between 120 and 150 μm. With no carrier gas flow, and a pressure of 1 bar, only 0.24 mass % yield of acetylene from coal was obtained at 1970K, with 0.57 mol % acetylene in the product gas. When the pressure was dropped to 0.1 bar, the yield rose to 2.27 mass % using the same feed rate, and to 3.7 mass %, with a concentration of 5.75 mol % for a larger feed rate. A hydrogen carrier stream improved yields and concentrations markedly. With a hydrogen flow, yields of 13 mass % were obtained, with concentrations of 1.1 mol % at 1 bar and 3.9 mol % at 0.1 bar. The acetylene obtained varied with the volatile content of the coal, the yield being smaller than the figures above for smaller volatile content. Heating times ranged from 0.6 to 8 ms.

2-D Low Pressure Electrical Discharges

Chemical reactions are sometimes initiated by means of a "glow discharge". This electrical discharge is normally operated with pressures lower than 0.1 bar, with large electrodes maintained at a sufficient temperature to emit electrons freely. It characteristically has a low current density, and has moderate potential gradients of around 50 v mm^{-1}. Chemical reactions carried out in such a discharge are largely initiated by the action of electrons which are not in thermal equilibrium with the gas molecules. The gas temperature is characteristically only several hundred degrees Centigrade, whereas the effective electron temperature is of the order of tens of thousands degrees Kelvin. As the electrons are the only component which is heated, from a simple view little energy is required to achieve a good concentration of active species for a desired reaction.

D1 Hydrocarbons

A glow discharge in methane at 0.05-0.07 bar was investigated by Shekhter of the USSR in 1935 (9), who reported a conversion to acetylene of 80%.* The concentration of acetylene in the product gases was 9 mol %, and energy use 11.2 kwh kg^{-1} acetylene.

Schoh, of Texas, developed a silent discharge process in 1943, which was sold to Esso in 1958. Miller (10) reported an energy use of 14 kwh kg^{-1} acetylene for this process.

* When the methane reaction to acetylene is discussed, the apparent degree of completion of the reaction $2CH_4 \rightarrow C_2H_2 + 3H_2$, based on the amount of the product acetylene, will be given.

Brooks, Hesp and Rigby (11) have carefully optimised a glow discharge reactor operated at abnormally high pressures, for acetylene yield and electrical energy use. Methane to acetylene conversion reached a maximum of 89% at 0.1 bar, falling to 53% at 0.5 bar. The minimum discharge energy consumption for an unheated methane feed was found to be 21 kwh kg^{-1}, which fell to 16.7 kwh kg^{-1} when the methane was preheated.

D2 Coal

Fu and Blaustein (12) reacted coal particles of size less than 70μm (-200 mesh) in a microwave discharge through hydrogen and argon mixtures. The maximum yield of acetylene was achieved for a coal with high volatile content, and with a quenching surface held at liquid nitrogen temperatures. The yield was 13.5 mass %, based on the mass of coal. No energy consumption figures were reported. Since the pressure was only 0.03 bar, the temperature of the coal did not exceed 1000K.

2-E Arc Discharge Devices

E1 Liquid Feeds

The earliest developments with electric arcs for acetylene production used liquid feeds. Carbon particles which were electrically conducting were immersed in a liquid hydrocarbon and electrodes placed within the bed of particles. Momentary arcs occurred between the particles when a sufficient potential difference was applied between the electrodes, and these arcs vapourised small amounts of liquid rapidly. The rapid quench of the gases which occurred when the local arc died, preserved

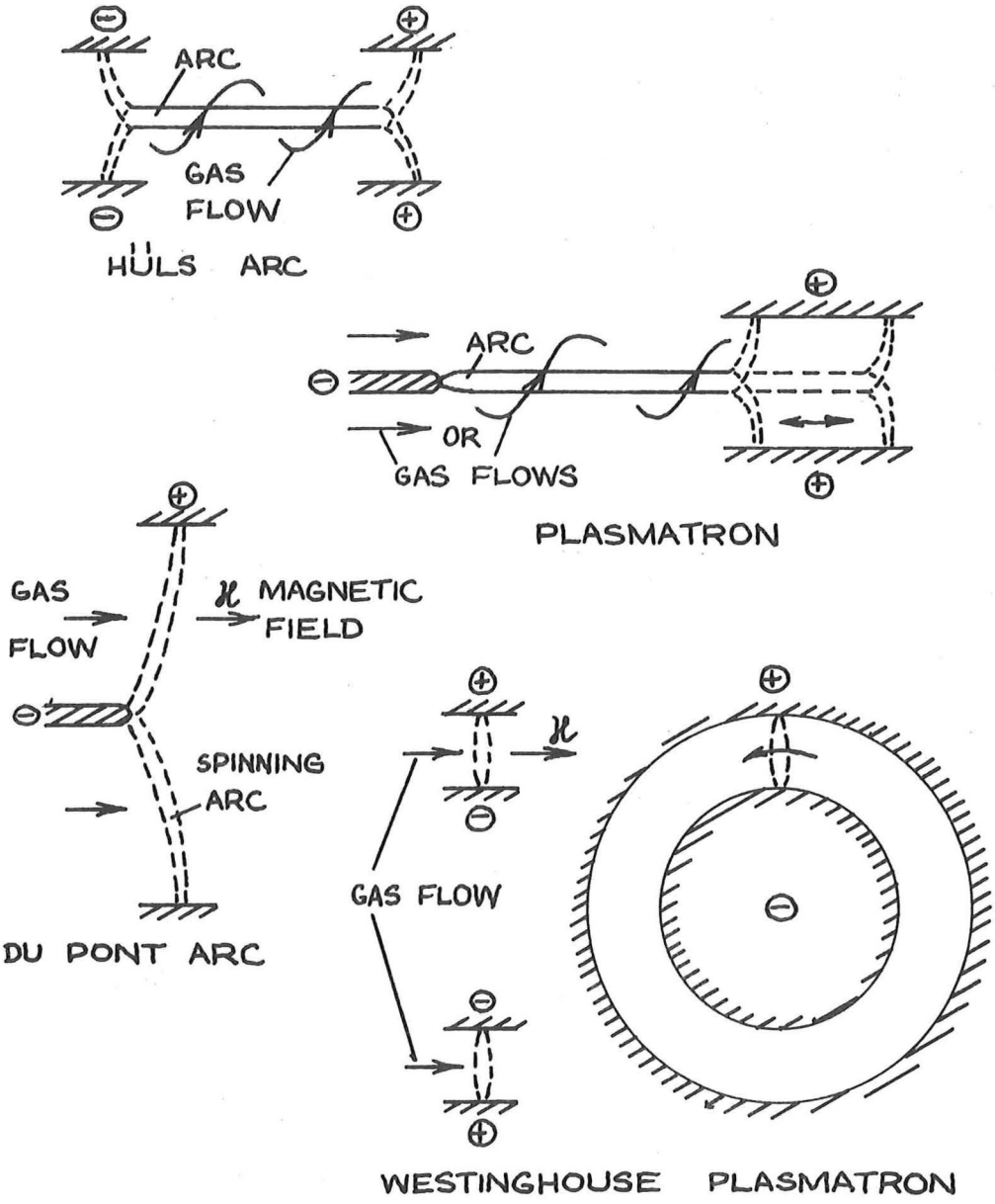


FIGURE 2.1 ARC CONFIGURATIONS

acetylene as a product.

Suits, in a 1944 U.S.Patent (13), described a reactor in which arcs of 60 μs to 10 ms duration occurred between lumps of coke 1.5 mm to 25 mm in diameter, submerged in oil. He reported an energy consumption of 7.8 kwh kg^{-1}, together with a product gas of 30 to 40 mol % acetylene. These attractive figures appear to be offset by the accumulation of soot in the liquid, probably causing shut-down before a good yield was obtained.

Kokurin and Obrezkov of the USSR (14), have determined the critical H/C atomic ratio of the liquid above which negligible soot is formed in such a reactor. They found that very little soot was formed when liquids were used in which the atomic ratio $H/(C-H) \geq 3$, and where oxygen was present, $H/(C-O) \geq 3$. Acetylene was formed with a yield of 65 mass %, with a concentration of 30 mol % in the off-gas. A variety of liquids were used, including alkenes, alkanes and ethers. No energy figures were reported.

Vozdvizhenskii (15) in 1954 reported a three phase discharge between carbon electrodes inserted in a bed of coke or coal immersed in hydrocarbon liquid. The power supply was pulsed for 1 ms at 0.1S intervals. In 1958 it was claimed (16) that this process produced acetylene for only 6.2 kwh kg^{-1}. However, Miller in the USA reported (10) in 1964 that a similar process tested by his company used 19 kwh kg^{-1} acetylene.

E2 Gaseous Feeds

Arc devices for the rapid heating of gaseous hydrocarbon feeds show three basic designs, as in Figure 2.1;

1. Hüls plant -

   hollow cathode and anode

   vortex stabilised

   arc stationary over most of its length

   anode and cathode attachments allowed to move

   gas flow parallel to arc

2. Plasmatron -

   hollow anode, rod cathode

   vortex or sheath stabilized

   arc stationary over most of its length

   anode attachment allowed to move, cathode attachment fixed

   gas flow parallel to arc

3. Du Pont and Westinghouse Electric plants -

   arc forced to move at right angles to its length by a transverse magnetic field

   anode attachment allowed to move

   cathode attachment either stationary or allowed to move

   gas flow across arc

E2/1 Hüls Plant

The largest commercial undertaking has been that at Hüls, in Germany, which has a capacity of 100 000 Mg yr^{-1} of acetylene, and has operated with some small modifications, since 1940. A variety of feedstocks are used, including refinery LPG, natural gas and light and heavy naphthas. The plant has 19 pairs of arcs, each of 5000-6000 Mg yr^{-1} capacity. Presumably the arc devices are operated in pairs so that one of each pair can have replacement electrodes fitted, and lie idle until fitting is required for the

other one. Each arc is about 1 m in length, is struck between two hollow iron electrodes, and dissipates 8.2 MW. Stability is achieved by the vortex about the arc created by tangential feed at the cathode. The feed gases are heated by movement through and around the arc to the anode, after which they are quenched by a liquid spray. Originally the spray was water, but recently a liquid hydrocarbon has been substituted (17).

With the hydrocarbon quench, one pass through the arc yields 35 mass % acetylene, 17 mass % ethylene, 10 mass % carbon black, with a remainder of hydrogen and some minor products. In practice, those hydrocarbons not converted to acetylene or ethylene are recycled to the arc, giving a concentration in the product gas of 16 mol % acetylene. Power use, as reported for the earlier practice at Hüls, was 11-13 kwh kg^{-1} acetylene for arc power, together with another 2 kwh kg^{-1} for purification. More recent figures for the plant (17) indicate arc energies of 9.5-10.5 kwh kg^{-1} acetylene. Replacement of reactor components contribute to running costs. Cathodes are replaced after 800 h, and anodes after only 150 h.

E2/2 Plasmatrons

Most of the effort made in the last decade in the development of techniques to produce acetylene from hydrocarbons, has been given to the device known as a "plasma jet" in the Western Countries and as a "plasmatron" in Eastern Europe. The author will use the term "plasmatron" since plasma jets, or jets of plasma, occur with many arcs irrespective of electrode configuration, and the latter term should not be confined to the

configuration of the plasmatron. Operation of the plasmatron consists of striking a direct current arc from a rod cathode to an orifice anode through which the working gas escapes. The cathode material is commonly tungsten, and the anode commonly copper, which is intensively cooled with water.

Tangential entry of the working gas at a high velocity into the arc chamber ensures that the arc remains centrally located as the gas spirals out, round the arc in the anode hole. This technique is termed "vortex stabilization". Another method of stabilizing the arc, called "sheath stabilization", is achieved by surrounding the arc with cold gas moving parallel to the arc along the walls of the arc chamber.

The arc in a plasmatron operates steadily to the eye, but when the gas flow is increased above a certain critical value, it has been found that the arc voltage changes from a steady value to a periodic fluctuating value, with period less than 1 ms. It has been shown (18) that this voltage behaviour corresponds to a change from a steady arc length, to a fluctuating arc length, with a moving anode arc attachment. The latter forms at the upstream edge of the anode hole, travels down with the outrush of gas, lengthening the arc until the arc is blown out. Simultaneously the arc attaches at the upstream edge, and the cycle is repeated. This rapid movement of the arc promotes mixing of hot and cold gases.

There have been numerous applications of the plasmatron to acetylene production from hydrocarbon gases. The majority use pure hydrogen or argon in the plasmatron itself, since hydrocarbons

cause troublesome carbon deposit unless special precautions are taken. The hydrocarbon is fed into the hot "working" gas flowing from the plasmatron, and the mixture quenched after suitable time for reaction.

In 1955, the German firm of Knapsack-Griesheim used hydrogen in a 4 MW plasmatron to pyrolyse propane (19). They reported yields of 80 mass % acetylene, 9 mass % ethylene, 7.3 mass % propylene and 3.6 mass % methane, based on the mass of propane, with a water quench. No soot was formed. Naphtha yielded 36 mass % acetylene, with a concentration of 13.7 mol % acetylene in the off-gas (20). Power consumption was about 11 kwh kg^{-1} allowing for purification.

Freeman and Skrivan (21) in 1962 investigated the power requirements for acetylene production using a 12 kW plasmatron. Methane was fed into either hydrogen or argon issuing from the device, and the mixture quenched by heat transfer to a cool tube. The maximum conversion to acetylene was 83%, found at the higher energy flows. An optimum specific energy use greater than 13 kwh kg^{-1} acetylene was found, which was not sensitive to moderate variations in power to feed ratio. No difference in yield was observed between hydrogen and argon runs. No concentrations were quoted. The authors studied a number of different mixing sections, and concluded that the mixing of a high velocity, high viscosity plasma stream and a low velocity turbulent gas was difficult to bring about.

Gulyaev, Kozlov and Polak reported (22) in 1963 the results of methane pyrolysis in a 15 kW argon plasmatron. They obtained

an 80% methane to acetylene conversion with a concentration in the argon-hydrocarbon product gases of 10.5 mol % acetylene. The mole ratio of argon to methane was 2. Arc power consumption was 13 kwh kg^{-1} acetylene. The product samples were withdrawn and quenched through cooled probes placed along the axis of the jet. A hydrocarbon content was found which was consistently low compared to that expected from the methane to argon ratio, and only approached the expected value some distance downstream. The authors attributed this to poor mixing of the argon and methane.

In 1962, Anderson and Case (23) fed methane into the hot hydrogen stream from a small conventional plasmatron, and analysed the total flow for acetylene after a water quench. Their work is interesting because they estimated the temperature of the hydrogen-methane mixture required for a minimum energy per unit acetylene. Various conversions were considered, each with a minimum feasible reaction temperature calculated from a simple thermodynamic treatment, and the reaction enthalpy and sensible enthalpy for temperatures above the minimum were considered. The thermodynamic calculations were based on 1951 data, and appear to allow for the existence of only C_2H_2, H_2 and CH_4. By this analysis, the minimum energy requirement was 14.2 kwh kg^{-1} acetylene, corresponding to a reaction temperature of 1700K. A step by step kinetic analysis was also attempted, using a single reaction step from methane to acetylene, and a single step for acetylene decomposition to the elements. The kinetic rates were extrapolated from data at temperatures of 1000-1700K for use at temperatures from 1800-2500K, and only methane, acetylene,

hydrogen and solid carbon were considered. From this simple analysis, some predictions were made.

Anderson and Case predicted a narrow maximum in the acetylene yield as a function of the hydrogen to methane ratio, for any given temperatures of the two streams. They argued that for a high yield sufficient methane should be present so that by means of the endothermic reaction to acetylene, the temperature of the reaction mixture be reduced to below 1800K. Excessive acetylene decomposition is thus avoided, since calculated reaction velocities are small below this temperature. However, if insufficient hot hydrogen is used, the calculations showed that the temperature of the mixture becomes too low for a high conversion to be achieved rapidly, and to attempt a high conversion, a long reaction time is required. With a longer reaction time, decomposition of acetylene is significant, reducing the yield. It is apparent that the final enthalpy and temperature depends also on the initial enthalpies of both streams, and so the methane to argon ratio for an optimum yield will depend on the initial states of methane and argon.

In Anderson and Case's experiments, a specific enthalpy of 640 kJ mol^{-1} was found for the hydrogen, and methane was introduced at room temperature. For these conditions, an optimum H_2/CH_4 mol ratio of 0.48 was calculated. The experiments were poorly documented, so that it is not clear whether experimental mol ratios differed from this value. The effect on yield of preheating the methane to 880-1100K was found experimentally to be equivalent to that of increasing the total

hydrogen enthalpy to the same extent, thus lending some support to the theory.

If one applies the theory to small regions of the gas mixture, it is seen that regions of gas which are hotter or colder than average, or differ in composition from the average, have a lower than optimum yield, and lower the overall yield. Thus rapid mixture is argued to be necessary for a high yield. Since the reaction velocities are calculated to be high before the drop of temperature, and slow thereafter, the acetylene yield is not strongly affected by what happens to the reaction gases after the temperature has dropped below 1800K. Thus the yield is argued to be almost independent of reaction time if it is greater than a certain short period, and not affected by the rate of quench. For example, if requirements are that greater than 80% of the methane be reacted, and less than 4% of the acetylene formed decomposed, the reaction time can vary from 0.08 to 1.3 ms. Two different lengths of reaction tube were used experimentally, to test the effect of changing reaction time. For each of the reaction mixture enthalpies used, no effect on yield was observed. Changes in quenching rates were not investigated. The theoretical curve of methane conversion as a function of specific enthalpy of the reacting mixture agrees well with the experimental findings, being within experimental error over the range between 30 and 90% conversion.

Anderson and Case reported experimental optimum values for methane conversion to acetylene of 76%, for acetylene concentration 15 mol % and for energy use 18.9 kwh kg^{-1} acetylene.

It is not stated, and one can only assume, that these figures refer to the same experiment. Diacetylene and ethylene were also produced in small quantities.

In 1964 a pilot scale application of a plasmatron by Magnetohydrodynamics Inc., of California, was reported (24). A single unit of 4000 Mg yr^{-1} throughput was operated with feeds ranging from methane to naphtha, with the "efficiency of the process" improving as the feed molecular weight was increased. With differing conditions and feedstocks, both acetylene and ethylene were formed, in a ratio of 0.1 to 10 or more. A cost study made by Fluor Corporation indicated that for a favourable Gulf Coast situation in the U.S., acetylene could be made for 11 U.S. c kg^{-1}, without credit for hydrogen and ethylene byproducts. No further details were given.

When methane is converted to acetylene, a large quantity of hydrogen is formed. Even when a plasmatron reactor is fed with a heavy naphtha (atomic H/C = 2), some hydrogen is formed from the reaction to acetylene. To reduce separation costs, it would be desirable to be able to return the product gas, stripped of acetylene, directly to the plasmatron as its working gas, without further separation of unconverted feed and byproducts. However, problems of carbon deposit on the anode orifice occur with only several per cent of methane in the hydrogen. In 1966, Colton patented a method to prevent this deposition (25), by vibrating the anode. Only an hour's operation was possible with 10 mol % methane in the hydrogen feed with no vibration, whereas with a small vibration

the anode remained clean. Using a 55 MW vortex stabilised plasmatron operating with a mole ratio of hydrogen to methane of 0.68, the production of acetylene amounted to 5.7 Mg h^{-1}. The methane to acetylene conversion was reported as about 80%, with an energy use of 9.7 kwh kg^{-1}.

Minc et al. (26) of the USSR investigated the effects of the following factors on the acetylene yield and power requirements of a methane fed plasmatron.

(1) number and position of methane inlet ports

(2) methane to hot gas ratio

(3) reaction time

A small plasmatron of 9 kW rating was used to heat an argon flow. The type of quench was not disclosed. Keeping all other conditions constant, experiments were compared where the methane feeder was changed from a single tube at 90° to the reaction tube, 5 mm downstream of the plasmatron nozzle, to four tubes at 90° to the reaction tube at the same position. The conversion to acetylene rose from 62 to 79%, and energy requirements dropped from 34 to 27.7 kwh kg^{-1} acetylene. Also keeping other conditions constant, with a single point feed, the distance of the quench from the methane feed point was decreased from 3.0 cm to 1.55 cm, with no effect on yields or energy requirements. With a four point methane entry and a methane port to quench distance initially of 5 mm, the points of methane entry were advanced upstream into the anode nozzle. The angle of feed unfortunately was also changed, from 90° to 30° to the axis of the nozzle. The combined effect of these changes, with other conditions constant, was to increase

the conversion to acetylene again, from 79 to 86%, and to drop the energy requirement from 27.7 to 24.3 kwh kg^{-1} acetylene.

From the first comparison, it appears that the better mixing achieved with four ports gives a higher yield. The second comparison supports the idea that within a certain range, differing reaction times have no influence on the yield. In the final comparison, no separation of the effects is strictly possible. If the shortened residence time still had no effect, the extra mixing caused by the rapidly moving arc around and downstream of the point of entry of the methane was likely to have improved the yield. It is interesting to note that no soot was formed when the feed was introduced from within the nozzle, apparently in contrast to what was found with feed entry downstream of the nozzle.

Minc et al. varied the methane feed rate, keeping a constant flow of argon from the plasmatron with a specific enthalpy of about 180 kJ mol^{-1}. With a feed of methane at room temperature, a narrow minimum was found around an argon to methane mole ratio of 3 for the energy required for acetylene production. This minimum was 16.8 kwh kg^{-1} acetylene, with a conversion to acetylene of 69%. The concentration of acetylene reached a maximum at this point, of 9 mol %. With a feed of 50-150°C boiling point petroleum fraction, both acetylene and ethylene were obtained, in concentrations of 10-13 mol % and 3-6 mol % respectively. The energy consumption was about 13 kwh kg^{-1} of acetylene and ethylene combined.

Amman, Timmons and Krukonis provided a scanty report in

1967 (27) of work with a small plasmatron in which methane was introduced into the plasmatron itself. The quench was achieved by mixing either cold hydrogen or helium with the hot methane. Differing power levels were used in the plasmatron, providing a range of specific enthalpy of the methane issuing from the device from 330 to 630 kJ mol^{-1}, corresponding approximately to temperatures between 2500 and 3300K. Methane conversions varied from 65% at the lower enthalpies to 80-100% at the higher enthalpies, with conversions presumably reported as a yield of acetylene. When low flows of quench gas were used, a large fraction of the products was soot, indicating a slow or incomplete quench. The use of helium in the place of hydrogen as a quenching medium gave slightly higher conversions.

In 1968, a report was published (28) of work by Kozlov et al. of the USSR in which methane was pyrolysed in a 30 kW plasmatron, run with two methods of arc stabilisation. Operating pressure was also altered.

It was found that changing from gas sheath stabilization to vortex stabilization did not materially affect the yield or energy use for acetylene production. For a reactor pressure of 1 bar, and a flow of hydrogen from the plasmatron with a specific enthalpy of 320 kJ mol^{-1}, an energy optimum for acetylene production was found at a hydrogen to methane mole ratio of 0.7. This optimum was 10.5 kwh kg^{-1}, at which a concentration of 12.9 mol % acetylene was found in the product gases, showing a 63% conversion of methane to acetylene. When the pressure was increased above 1 bar, less acetylene was formed.

Pressure/bar	1	3	6
C_2H_2 Conc./mol %	11.3	8.7	7.5

Ethylene increased with pressure, to 2.5 mol % at 6 bar. Some trouble with burnout of the anode was experienced at the higher pressures. The plasmatron was equipped with a water spray quench, and methane was introduced radially at the anode nozzle exit into the hydrogen stream. It appears that more than one port was used.

A plasmatron development which has important commercial advantage is the design of cathode and arc chamber which permits the sole use of methane in the plasmatron over extended periods. As no recycle of hydrogen is then necessary, the cost of separation is avoided. The operation of a 250 kW pilot plasmatron designed to do this was reported by Sidorov, Il'in and Polak of the USSR, in 1968 (29). A finger cathode and a nozzle anode were employed as usual, but the cathode was also hollow, and up to one half of the total feed was introduced through the tip of the cathode. The rest of the feed was brought through the perimeter of the arc chamber. A petrol vapour quench was used, which was situated at the exit to the anode nozzle.

The feed used was a natural gas, with 90 mass % methane and 5 mass % nitrogen. The latter was added for some purpose, probably to reduce the arc voltage. Total pressure was varied from 0.5 to 1 bar. Energy use was given as 2.5 kwh m^{-3} (standard) of feed, and a product was obtained having the composition in mol %; 16.6 acetylene, 0.76 ethylene,

0.33 diacetylene, 0.2 profyne, 0.1 vinylacetylene, 0.05 benzene and 0.19 hydrogen cyanide. It is estimated from these figures, by a mass balance over the plasmatron, that 52% conversion of methane to acetylene was found, with an energy requirement of only 8.7 kwh kg^{-1} acetylene.

A recent review of plasma chemical technology by Polak and Vurzel (30) published in 1970 outlines the best Russian results for the acetylene reaction from methane in a plasmatron. "At both the laboratory and industrial scale", at energy optimal conditions, the conversion of methane to acetylene was 80%, the acetylene concentration in the product 16 mol %, and energy consumption was 9 kwh kg^{-1} of acetylene. It is reported that the content of higher acetylenes was low and decreased with increasing size of the plasmatron reactor. The process was improved if a hydrocarbon (e.g. propane, butane or gasoline) was used in a quench. Some ethylene was formed if this was done, as well as extra acetylene, which brought the acetylene concentration in the product up to 23 mol %.

E2/3 Du Pont and Westinghouse Electric Plants

It is desirable from an economic viewpoint that the gas to be pyrolysed be the arc gas, for extra gas separation costs are avoided, and the energy is dissipated directly into the feed. With stationary arcs, however, poor contact between the arc and the bulk of the feed results in uneven heating, with consequent sooting and low acetylene yields. The Du Pont and Westinghouse Electric Companies in the United States have both employed magnetic fields in large arc reactors in order to move the arc

rapidly through the gas feed. This motion mixes the gas of the arc at 10000 to 12000K with the cool gas surrounding it to achieve a uniform intermediate temperature.

The Du Pont development was described in 1965 in a U.S. patent (31). The cathode was centrally located in the device, and was a water cooled graphite rod. This was surrounded by a water cooled tube which was the wall of the arc chamber, and which served as an anode. An arc was struck from the cathode tip to the wall, and rotated about the cathode by a magnetic field, with an angular velocity of 4000 to 8000 revolutions per second. A primary feed of methane was introduced upstream of the arc, and a secondary feed of propane or gasoline brought in downstream of the arc. This secondary feed partially quenched the hot gas, and provided more acetylene. A final quench was given by a water spray positioned further downstream. Operating pressures were recommended between 0.13 and 0.46 bar, for better yields were obtained at these lower pressures, and less soot was formed. Average temperatures were reported at different positions. These were 2300-3100K after the arc, above 1600-1900K after the secondary pyrolysis, and less than 600K after the water quench.

Two sizes of reactor were constructed, one of which had twice the dimensions of the other. The smaller reactor consumed 26 kg h^{-1} of methane, and 52 kW, whereas the larger reactor consumed 370 kg h^{-1} methane (14x) and 520 kW (10x). It was reported that the reaction times from contact with the arc to quenching, were carefully controlled in the range 1.3-1.5 ms for the small reactor and 1.1-1.2 ms for the large reactor.

If one assumes similar temperatures for both reactors in order to check these figures, a reaction time of half that of the small reactor is indicated for the large reactor. A table of results is presented below for small and large reactors, with and without secondary feed.

Du Pont Arc Reactor for Methane Pyrolysis

Methane conversion to acetylene and energy for acetylene production kwh kg^{-1}	Methane feed	Methane and secondary
Small reactor	80% / 15.4 kwh kg^{-1}	77.8% / 13.2 kwh kg^{-1}
Large reactor	73.7% / 11.7 kwh kg^{-1}	69.4% / 9.5 kwh kg^{-1}

The improvement shown in the table of power used with the increase in size must result from a smaller energy loss to the walls and electrodes of the reactor. In the small reactor, 36% of the arc energy was delivered to the walls and electrodes, compared to only 17% for the large reactor.

The Westinghouse Electric arc device was described in 1966 in a Westinghouse publication (32). The arc was struck between two torroidal copper electrodes, and moved sideways along the electrodes by a magnetic field. It thus spun in a circular path following the electrodes, with an angular velocity of about 10^3 revolutions per second. Gas feed was introduced radially through the spinning arc towards the centre of the device, was heated and mixed by the arc, and passed out along the axis. Arc stability was achieved only by reducing the electrode-electrode gap. For a 3 MW unit, this gap needed to be less than 100 mm.

Arc heaters of this type have been built and operated for

ratings from 2 to 20 MW, and in 1966 were being designed for the 100-300 MW range. Direct current, single phase alternating current, and 3 phase alternating current power have been used. Since there is no advantage in using direct current with this type of arc heater, and rectification from alternating current is normally needed, the larger units are operated with 3 phase power.

A 3 MW unit was used for the reaction of methane at rates of up to 2 Mg h^{-1}, and with specific enthalpies of gas before quenching from 70 to 700 kJ mol^{-1}. Westinghouse engineers reported an energy use of 14.7 kwh kg^{-1} acetylene, a product composition of 9.5 mol % acetylene, and only a 27% conversion of methane to acetylene. An energy requirement of only 6 kwh kg^{-1} was also reported, but it was indicated that this needed further experimental verification. The acetylene analyses were obtained from gas withdrawn through cooled probes, and were probably non representative of the total flow. When methane was heated in the device, the proportion of the arc power which was lost to the reactor body showed a minimum of 21%. When comparing the Du Pont and Westinghouse yields and energy losses, it appears unlikely that the low value of 6 kwh kg^{-1} is accurate.

E3 Coal feeds

The use of carbon and hydrogen from a solid feed for the production of acetylene poses some special problems. The most convenient solid feed is coal, and the more easily reacted portion

of coal is that which is "volatile" or easily removed from the solid by heating for some time up to 1200K. This part has a higher H/C ratio than that of the parent coal, which has a ratio of about one atom per atom for a sub-bituminous coal. The yield of acetylene is thus restricted at moderate temperatures to about 25% of the original mass of coal. To use the "fixed carbon" at any appreciable rate requires a temperature sufficiently high to vapourise carbon. This temperature is most conveniently obtained with an arc.

Bond et al. (33) fed coal in pulverised form into a conventional 12 kW plasmatron. The variables studied were

(1) Coal particle size

(2) Coal volatile content

(3) Particle residence time

(4) Plasmatron arcing gas

Argon, hydrogen and nitrogen were used as the arcing gas. Coal was fed as a fluidised flow of particles. A direct feed into the plasmatron arc chamber was attempted, but severe erosion of the cathode resulted. Introduction of the coal through the anode wall was found to be satisfactory.

The coal particle size was varied from 590 μm down to less than 10 μm, in 9 narrow size ranges, and sufficient gas was used so that the particle residence time was about 1 ms from feed to quench. Argon was used at first. It was found that coal particles larger than 200 μm were scarcely affected by passage through the reactor, whereas smaller particles yielded progressively higher yields of acetylene until a size of 50 μm was reached, at

which the acetylene formed amounted to 20% by mass of coal fed. The yield fluctuated somewhat around 20% for sizes below 50 μm, and varied from 18 to 28% for sizes below 10 μm.

A range of coals were tested, with volatile matter varying from 6 to 55 mass % as determined by BS 1016. The figures above refer to a high volatile coal. When an argon stream was used to carry particles of 53 to 74 μm size so that a residence time of 1 ms was obtained, the yield of acetylene was proportional to the amount of volatile matter in the coal. When based on the mass of carbon originally present in the volatile matter of the feed, the mass of carbon found in the product acetylene corresponded to a 40% conversion. The view that only the volatiles were reacted to any appreciable extent, was supported by the very low yields observed from low volatile feeds such as carbon black, and by the fact that even with a hydrogen-rich plasmatron gas, no acetylene yields were found which were significantly above that possible from the volatile matter.

The composition of the plasmatron gas was changed from the 100% argon used in the majority of runs. Hydrogen, nitrogen and methane were added to the argon flow in increasing amounts. The addition of hydrogen caused a marked increase in voltage, and the current was accordingly reduced so that comparisons could be made at constant power input. Acetylene yield increased with increasing hydrogen content up to 0.15 mol H_2 per mol of mixture, but dropped for higher hydrogen contents. Bond et al. explained this drop as being caused by poor contact of the coal particles with the contracted arc which occurs in

hydrogen. When nitrogen was added, hydrogen cyanide was formed in preference to acetylene, with the total yields by mass of hydrogen cyanide and acetylene equalling the previous acetylene yield with hydrogen added. Methane was also added to the argon flow, and 60% was converted to acetylene irrespective of whether coal was present or not. The coal conversions were similar to those with hydrogen as an additive.

Efforts were made to vary the residence time of the coal particles in the hot plasma. The flow rate of gas, and the length of tube were varied. Little change of results was found for different lengths of tube with other conditions constant, showing that the residence time was not critical, for a limited range above and below 1 ms. Quenching was achieved in these experiments simply by directing the jet of hot gases into a large vessel containing cold product gas. No tarry products were formed, and the solids which remained contained from 5-20 mass % volatile content. Some interesting observations were made on the product carbon. Much of it was in the size range 60-90 nm if the feed was a coal. On the other hand, low volatile feeds passed through almost unchanged in size. The authors attributed the small size of the coal residue largely to shattering caused by the rapid release of volatiles, but conceded that some vapour phase formation of soot from the decomposition of hydrocarbon molecules, may have occurred.

Bond et al. reported a maximum concentration of acetylene in the product gas of less than 1 mol %, an energy use of about 800 kwh kg^{-1} acetylene, and 33% of the mass of carbon in the coal appearing

in the acetylene.

Kawa, Graves and Hiteshue (34) investigated the reaction of pulverised coal in argon and argon-hydrogen streams with a 28 kW plasmatron. Their experiments were of little value, for analysis of the product gas was carried out after bubbling the gas through a large trough of water, with no apparent allowance for the acetylene dissolved into the water. Very little of the volatile matter in the coal was reacted, for a volatile content of 33 mass % was found in the solid residue, compared to 38 mass % in the coal. This could be explained by a poor contact between the arc and coal particles, or a shorter heating time after the stream had left the plasmatron. The feed system was superficially the same as that used by Bond, in that a fluidised particulate coal was introduced through the wall of the anode nozzle. The quench and cooling of the particles may have occurred more rapidly than in the work of Bond, for the particles were collected in the water trough. Not sufficient information about dimensions and flow rates was given to make any more detailed comparison.

Kawana et al. (35) obtained acetylene from the pyrolysis of pulverised coal in an argon plasma flow from a plasmatron. They used argon with a specific enthalpy of 170 kJ mol^{-1}, and fed coal in sufficient proportion so that the ratio of carbon atoms in the coal feed to the argon atoms from the plasmatron was about 0.1. Their coal contained 45 mass % volatile matter, and under the above conditions, yielded acetylene to the extent of 24% by mass of the coal. Thus only 60% of the

carbon in the volatile matter was required to be reacted to account for the acetylene found. The energy requirement was reported as 135 kwh kg^{-1} acetylene.

A major effort to use coal as a raw material for acetylene production was initiated in 1966 by a $2 000 000 contract between the U.S. Bureau of Mines and A.V.C.O. Space Research Centre, Massachusetts, to investigate the use of arc devices tailored in this specific problem (36, 37). Three designs were evolved in succession, and tested, using a 100 kW power supply. The first design was based in principle on the "high intensity" carbon arc, the name given to the arc behaviour observed when the current density at a carbon anode is sufficiently large to erode the carbon at an appreciable rate. Krukonis, Gannon and Schoenberg of AVCO Corporation operated an arc between a rod cathode, which was graphite, and a "rod" anode, which was 25 mm in diameter, and consisted of powdered coal driven up through a water-cooled copper tube. The cathode was held vertically above the anode surface coaxial with the anode, and less than 10 mm from it. As the coal approached the arc, coking occurred, and the temperature rose until the coked material could carry current from copper walls to the seat of the arc, wherever it happened to be, on the face of the coal anode. It is questionable whether the surface of the anode received enough energy to vapourise appreciable quantities of carbon in the "high intensity carbon arc" sense, for a maximum arc power of only 40 kW was reported with this configuration. Assuming an arc voltage of 40 volts in hydrogen for the short path used, a total current of 1000 A,

and a current density of 50 A cm^{-2} is calculated. The anode was surrounded by a cooled copper tube almost flush with the arcing face, a situation which is expected to draw more energy away from the anode face then if the anode was free standing, as is normally the case with a carbon arc. If one assumes that the radiation loss from the front face of the anode is the same in this device as in a free standing graphite anode (1.2 kW cm^{-2}), and the conduction loss of energy axially into the anode is the same in both cases, then the radial energy flux from the anode will make the difference between the two situations. Assuming a thermal conductivity of graphite, and a temperature of 4000K at the centreline, this writer estimates an energy flux of about 6 kW cm^{-2} for the "coal" anode, compared to the 1.2 kW cm^{-2} radiation from the side of a free standing anode. This argument, together with the fact that a current density of about 100 A cm^{-2} is normally needed on the anode of a carbon arc for appreciable ablation, indicates that insufficient energy was present at the anode to justify the high intensity description.

Practical difficulties with this first design prompted an end to work with it. These difficulties centred on the front rim of the anode, which was shielded with graphite "or other material". Nonetheless, it is instructive to follow the details of the work with the first design.

About 11 kg h^{-1} of crushed, air dried coal, typically of 1.4 to 2.4 mm size (-8+12 mesh), was fed vertically upwards by a ram through a 25 mm diameter water cooled copper tube 0.6 m in length, directly into the arc, which played on the front face of

the coal. The graphite cathode, a rod of 16 mm diameter, was held from the side of the reactor. The hot gases and char were cooled rapidly by injection of hydrogen or argon above the cathode, and were sampled above this again, for analysis.

When argon was used as the "quenching" medium, the yield was only 2.5% at 20 kW power input, and 5.5% at 40 kW, where the yield was expressed as the mass of acetylene found per unit mass of carbon fed in the coal. The energy requirements were constant with varied power input, at about 86 kwh kg^{-1} acetylene. It was reported that from 15 to 20 mass % of the coal was gasified, and the char analysis showed a ratio of hydrogen to carbon atoms of 0.01 to 0.03, compared to 0.86 in the coal. Thus the volatile matter was effectively driven off, using this anode design.

When hydrogen was used as the "quenching" gas, the acetylene yields rose significantly, to 6% at 20 kW, and 13.5% at 40 kW. The energy requirement dropped to about 35 kwh kg^{-1} acetylene for the same operating conditions as for the 86 kwh kg^{-1} figure given above with an argon quench. With hydrogen as the quench gas, a char from a previous high power run was used as a feed in place of the coal. The arc was more erratic presumably because the particles did not fuse to form a continuous current path. With a char containing 0.1 mass % hydrogen, the yield of acetylene was about 5%, showing that in this instance, some of the "fixed" carbon reacted with the "quench" gas. It is likely that the char was broken down finely, or even vapourised, to give this extent of reaction in such a short time. It is also likely that this carbon breakdown occurred to some extent with the coal feed.

Krukonis et al. in fact assume that the fixed carbon in their coal feed reacts to the same extent as does a char feed, but this is not justified, as the splitting of the coal with large quantities of volatiles released would cause a difference in the reactants present, and their concentrations.

The observations on the solid residue, and on the anode after a run had stopped, are of interest. It was found that a char layer of 6 to 13 mm in depth existed on the top of the anode. Since the linear velocity of the coal was 10 mm s^{-1} when the arc was running, then if one assumes that the progression of coking into the coal was negligible after the experiment was stopped, a heating time for the coal from 700 to 4000K is found to be about 1s. Considering the coke as graphite and noting the enthalpy change, one can calculate a rough estimate of thermal conductivity. This writer finds a value of 300 J $m^{-1}s^{-1}K^{-1}$ which is high compared to that of graphite (13 J $m^{-1}s^{-1}K^{-1}$ for temperatures $>$ 2800K and 150 J $m^{-1}s^{-1}K^{-1}$ at room temperature). It is unlikely that the low density coke would have a thermal conductivity as large as that of graphite. The discrepancy appears to lie with the assumption about the progression of coking. Coking of the anode coal after the run was stopped is indicated, so that the reaction zone in the coal was likely to be considerably less than the charred zone found after the run.

This char showed a very low hydrogen content, and contained spherical soot particles of 20-30 nm diameter in the voids within the char, indicating a rapid gas-phase breakdown of hydrocarbons to carbon (and hydrogen) within the coal. Any

hydrogen formed by this means may react with the char or soot when these have entered the arc. Soot particles of the same size as those in the char voids were found on the walls of the reactor, and analysis of these particles showed 5-6 mass % ash, compared to the 5 mass % ash in the coal. It is highly likely that the soot formed from the gas phase, so that the ash must then have been vapourised also. Temperatures at coal particle surfaces sufficient to boil the ash were probably reached.

Krukonis et al. explained their low acetylene yields ($\leq$ 13.5 mass %) by the cracking of volatile matter before it reached the anode surface, together with incomplete contact between the arc and coal. As all hydrocarbons pyrolyse to carbon and soot at intermediate temperatures between that of the coal and the arc, the first point raised above is equivalent to the assumption that a lower yield is obtained by the reaction of carbon and hydrogen in these conditions than is obtained by the reaction of the hydrocarbon molecules in the volatile matter. This assumption will be discussed in a later chapter. Krukonis et al. reported that frequently a third of the coal went through the reactor "unconverted", suggesting that it was not even coked.

The second design which was worked on attempted to give a shorter heating time for the coal. A graphite rod connected to the positive terminal of the power supply was placed centrally in the anode tube so that its tip was just below the level of the coal particles. These were partially fluidised with hydrogen, and fed upwards into the arc. However, much of the coal "remained unreacted", indicating poor contact with the arc.

A third design was used, which aimed at both a short heating time and efficient contact between the arc and the coal. A rotating arc similar to that used in the Du Pont reactor was devised. An axial magnetic field rapidly rotated an arc anchored on a central graphite cathode within a coaxial circular anode. The rotation of the arc was sufficiently rapid so that coal particles fed through the path of its sweep were effectively contacted. The coal feed was in a direction vertically downwards through a restricted hopper tube, with hydrogen flowing also through the coal bed into the arc.

The first attempt at using this design was with a reactor with a cathode of 10 mm diameter which was placed centrally in the coal, and extended down to the centre of an anode ring of 50 mm inside diameter. An arc gap of 20 mm was thus obtained. This configuration was limited by the low hydrogen flow which could be tolerated without extinguishing the arc. With the low flows of hydrogen, heat transfer back to the coal bed occurred, and coal particles fused together before reaching the arc. The investigators attributed the low yields obtained and the copious quantities of soot found on the reactor walls to the high enthalpy of the hydrogen. In view of Anderson and Case's analysis, this may be explained by the consequence that the mixture remained for a time at sufficient temperatures to cause appreciable decomposition of any acetylene formed. Observed yields of acetylene were 3%, and energy consumption was about 130 kwh kg^{-1} acetylene.

The diameter of the inside of the anode ring was reduced from 50 to 38 mm, reducing the arc gap from 20 to 14 mm.

This was sufficient to increase the stability of the arc so that lower power levels of 30 to 40 kW and higher hydrogen flows could be used. An energy requirement of 55 kwh kg^{-1} acetylene was obtained. The feed size range was then changed from 0.7-1.0 mm to 150-250 μm, with almost no observed change in the yield or the energy consumption, indicating that the important reactions taking place are not dependent on the original carbon surface area, and may be gas phase reactions.

All the developmental work discussed above on the AVCO project was carried out with a total pressure of 1 bar. Krukonis, Gannon and Schoenberg tested their rotating arc arrangement with a pressure of 0.2 bar, with the rationale that arc power and hence specific gas enthalpies would be reduced. A pressure of 0.2 bar was easily reached with a steam jet ejector pump. Yields were increased significantly. For the same feed rate and power level they rose from 3-5% at 1 bar to 13% at 0.2 bar. The energy consumption dropped in the same comparison from 55 to 20 kwh kg^{-1}. Note should be taken here, that as well as reducing the pressure, the cathode was also changed in position. Instead of pointing downwards from the centre of the coal feed, it now was below the anode, still lying along the axis, but with its tip pointing upwards facing the coal feed. The cathode end occupied 7% of the area inside the anode ring, so that some loading of coal onto the cathode tip may have altered the average residence time of coal particles in the arcing zone. It was reported that soot formation was much reduced at the lower pressure.

A hydrogen flow for quenching the hot gases from the arc

region was then installed, and the rate of hydrogen flow to the arc varied for a given coal feed rate. The acetylene yield reached 18% by mass of coal fed, for power inputs related to the hydrogen fed giving gross specific enthalpies for the hydrogen of 105 kJ mol^{-1} or more. The coal feed rate was next varied. The acetylene yield dropped from 18 to 7 mass % for a two-fold increase in feed rate, and the energy requirement reached a shallow minimum of about 14.5 kwh kg^{-1} acetylene. The acetylene concentration showed a flat maximum of 8 mol % of the product gases. This figure as reported is somewhat misleading, for a mass balance shows it to be calculated on a quench-gas free basis. No mention was made in the AVCO report of the amount of quench gas used.

A more recent report on the AVCO project (38) which precised a paper presented at the American Chemical Engineering Symposium in 1970, (39) gives the present achievements of the process. Using a secondary feed of coal downstream of the arc to increase the amount of acetylene produced, as well as partially cool the gases from the arc, 30 to 35 mass % yield of acetylene was obtained, with an energy requirement of 8.8 to 11.0 kwh kg^{-1} acetylene. A hydrogen stream was used at the same time, for quenching purposes. No enough detail was given (38) to view these figures critically. Some studies with the hydrogen isotope deuterium indicated that the quench gas took part in the reaction.

The 1969 report (36) mentioned a design and costing analysis on projected industrial-sized installations of the coal-arc reactor, carried out by Stone and Webster Corporation.

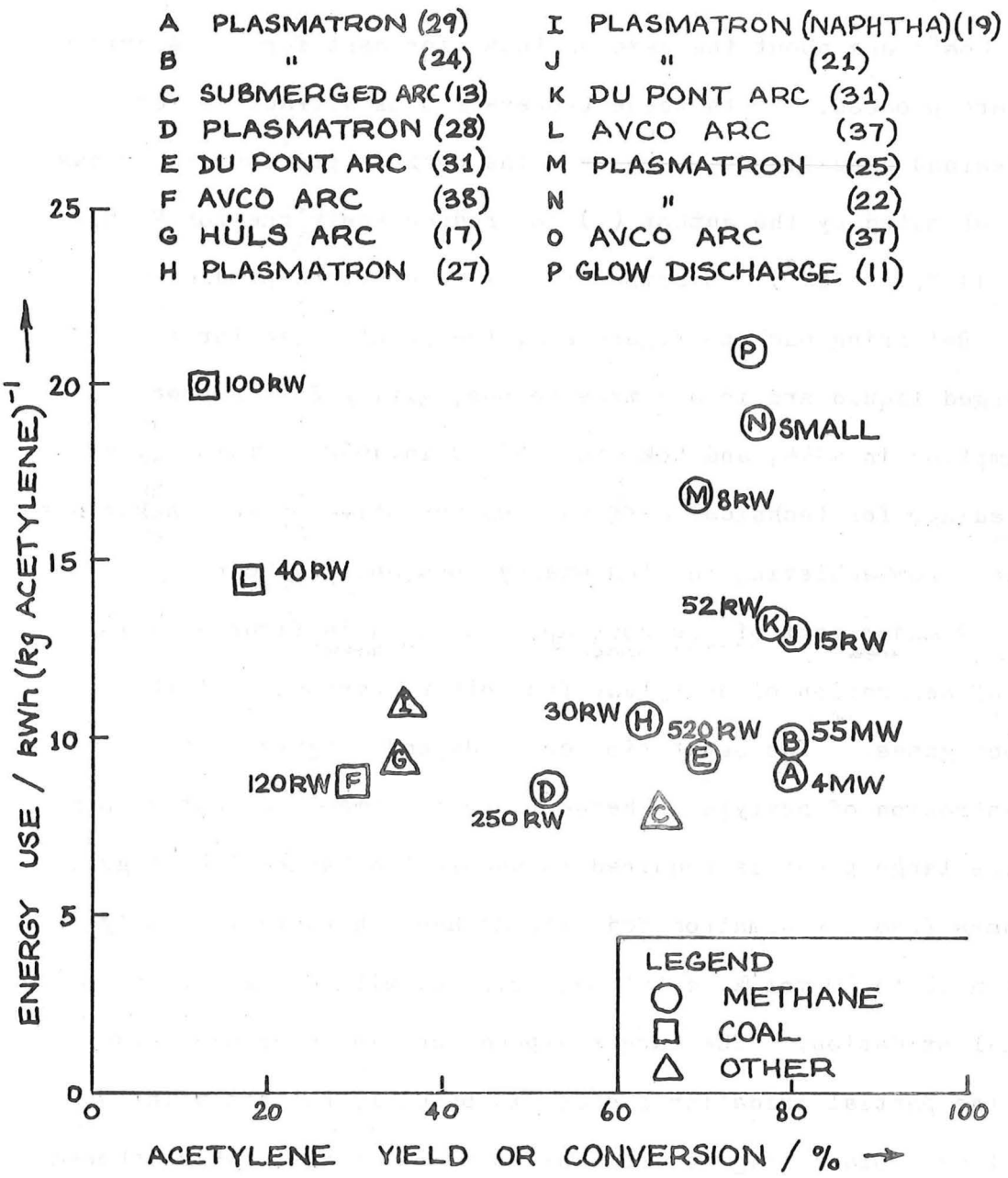
This analysis indicates (38) that acetylene could be sold for 11.5 U.S.c. kg^{-1} (5.3 c lb^{-1}), presumably in the more favourable locations in the United States.

2-F A Comparison of Methods for Acetylene Synthesis

For those processes discussed in this chapter which depend heavily on electrical energy, a rough economic comparison consists in a comparison of the energy requirements for production of a unit mass of acetylene. Another broad comparison may be made based on the yield, or mass of acetylene produced per unit mass of feed. In figure 2.2, the energy requirement is shown for economic and nearly economic processes, against the yield of acetylene. Whether the figures shown are economically competitive with other methods of acetylene or ethylene manufacture depends on the cost of power and raw material, among other things which are peculiar to the location. The Hüls plant has been operating in Germany since 1940, and at the recently improved energy use shown, must be economic in the German context. In 1970, Vurzel and Polak (29) compared the economics of the plasmatron with those of the Hüls electrocracker, and with the B.A.S.F. partial oxidation process - all presumably under Russian conditions. All processes were fed with methane. The Hüls process acetylene costs 110% of that from partial oxidation, whereas the plasmatron acetylene costs only 65%.

In the United States, the partial oxidation of methane produces acetylene which is generally costed at 17.5-20 U.S. c kg^{-1} (8-9 U.S. c lb^{-1}). If one regards that Vurzel and Polak's relative costs apply to the American situation, then in the U.S.

FIGURE 2.2 ENERGY AND RAW MATERIAL EFFICIENCIES OF ACETYLENE MANUFACTURE



acetylene from the plasmatron is costed at 11.5 to 13 U.S.c kg^{-1} (5.2 to 5.9 U.S.c lb^{-1}) acetylene. It is interesting to see that these costs are about the same as those forecast for the American coal-arc process. Both these processes look attractive for New Zealand conditions, where even the carbide process, which has been estimated by the author (1) to produce acetylene for 24 N.Z.c kg^{-1} (11 N.Z.c lb^{-1}), is competitive with ethylene production.

Referring back to figure 2.2, the point given for the submerged liquid arc is a composite one, giving Suit's power consumption in 1944, and Kokurin's yield in 1962. This may be misleading, for technical difficulties may still prevent Kokurin's process from achieving the low energy consumption shown.

A major part of the cost not indicated in figure 2.2 is that of separation of acetylene from other components of the product gases. The separation costs depend largely on the concentration of acetylene, being large for small concentrations because large plant is required to handle the large flow of gas. Offgases from a plasmatron fed with methane characteristically contain 16 to 20 mol % acetylene, compared with 8 mol % from partial oxidation. The larger expenditure in separating plant with the partial oxidation process is probably reflected in Vurzel and Polak's figures for the total plant cost, which showed that the cost of the plasmatron complex was only 60% of that based on partial oxidation. The major difficulty facing the AVCO workers in reducing their acetylene costs still further, appears to be the cost of separation, for their concentrations have been only 6 mol % when allowing for a minimal hydrogen flow for quenching.

This quenching flow used by the author is 0.5 mol H_2 per mol C. Any improvement in operating costs would be most likely to come from an increase in the low acetylene yields.

To provide some points to better design and operation of a coal, or coal and natural gas fed arc reactor, the more successful findings of the literature of this chapter are summarised below.

2-G Pointers for Optimizing Acetylene Production

G1 Scale

In general, an increase in size of an arc reactor from a laboratory model of 50 kW rating or less, improves the energy use, as can be seen from figure 2.2. Once the device has reached a size with a rating of several hundred kilowatts there appears to be no improvement with size, at least for those reactors which are gas fed.

G2 Pressure

Both the Du Pont reactor using methane, and the AVCO coal fed device, were run at absolute pressures in the range 0.1 to 0.2 bar to achieve optimum yields and energy use. It was noticed that much less soot was formed at the lower pressures than at a pressure of 1 bar, perhaps indicating that lower pressures are less favourable for the breakdown of hydrocarbon molecules to the elements. No work has been reported with plasmatrons at pressures below 1 bar, presumably because operation without soot formation can be achieved at a pressure of 1 bar (25). For pressures above 1 bar, the acetylene yield

from a plasmatron dropped off, according to Kozlov (27).

It appears that for a coal fed process, pressures of 0.1 to 0.2 bar are preferable. Further gains in acetylene yield may be made by operating the heating and quenching steps at two different pressures, with the lower pressure in the quench step where lower reaction rates are desired. With such a hot stream this is difficult. If a suitable material was found, a sonic nozzle could be constructed, across which the pressure drop required could be maintained by pumping. As internal energy would be lost by expansion through the nozzle, a rapid cooling would accompany the expansion, providing an effective quench.

G3 Mixing

Anderson and Case (22) argued that for the case of a methane feed, in order to avoid excessive soot formation, temperatures of the hydrocarbon mixture just after the arc must lie above 1800K by a certain margin so that the endothermic reaction to acetylene will bring the mix temperature to below 1800K rapidly. They pointed out that good mixing is required between the hot gas and the heated gas, so that regions do not occur where a higher than average temperature causes rapid decomposition of acetylene.
Minc et al. (25) showed experimentally the need for good distribution of reactants for high yields. It was shown by the experiments of Gulyaev et al. (21) with a plasmatron, that the mixing of a cold low viscosity stream of gas with a high velocity jet of plasma, where viscosities are about the same as that of water, is a difficult task to achieve.

Where the arc is struck in the hydrocarbon feedgas itself, mixing of the arc gas which is commonly at temperatures from 7000 to 12000K, with that surrounding it, is likely to be even more critical. Not only can localised decomposition occur, but large parts of the gas could remain unheated. What is needed is a definite mixing mechanism very close to the arc, such as a rapid and frequent movement of the arc, or induction of surrounding gas by electrode jets. If a solid feed such as coal was used in an arc reactor, similar requirements would apply to the volatile matter released from the coal. The reactions with the solid carbon remaining, presumably being a slower surface reaction of some kind, would need extraordinarily efficient mixing with the arc for either vaporization or reaction with hydrogen bearing gases to occur.

G4 Reaction Time

One can divide the time taken for material to pass from initial contact with the arc to where its temperature has been reduced to below 800K, into a heating period and a cooling period. The heating period is accompanied by chemical reactions towards equilibrium concentrations of hydrocarbon species at high temperatures. The quench period on the other hand, is required to be much shorter in order that chemical equilibrium is avoided, for acetylene can be broken down almost completely to the elements in the intermediate temperatures. For a gas reaction with a plasmatron, it has been found that the reaction time before quenching can vary from 0.5 to 2 ms with no effect on

yield. This suggests that chemical equilibrium may have been reached at the higher temperature. It is possible that the lower practical limit on this time is due to the process of heating and mixing, rather than reaction kinetics.

With conventional methods of heating solids, the heating time to bring a solids feed to reaction temperature would be an order of magnitude larger than those heating times found with gases. However with dissociated and ionised gases, chemical recombination and electron bombardment can improve the energy transfer to the solid. Also if a brittle solid such as coal is heated rapidly, it can shatter to very fine particles and thus expose more surface for heat transfer.

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DESIGN OF A SMALL SOLIDS-GAS-ARC CONTACTOR

CHAPTER 3

Contents

3-A Design Criteria

It has been shown in chapter 2 and appendix 1 that for the cheap production of acetylene from any feedstock, an appreciable part of the feed must be converted to acetylene, the energy use for a given amount of acetylene must be low, and acetylene must be produced in sufficiently high concentration. At present world prices, these parameters roughly need to be $>25\%$ yield, <11 kWh (kg acetylene)$^{-1}$ and >5 mol % respectively. At the design stage, it was seen that the yield and energy use could be considered as design criteria, in the light of the existing knowledge. The problem in this work then became "the efficient reaction of coal to acetylene", efficient in both energy and coal use. It appeared that the achievement of sufficient concentration of acetylene would follow the solution of this problem.

A1 Yield

Acetylene has been obtained by several methods from coal;

some methods have been detailed in chapter 2. The passing of pulverised coal through a heated tube, or into a plasma stream from a plasmatron, appears to remove and react the volatile matter in the coal, but leaves the "fixed carbon" as a char. A temperature of about 1800K is sufficient for the volatiles to react, but temperatures higher than this are required before solid carbon will react appreciably in a hydrogen-rich environment. If the rate of reaction with the solid is too slow at any temperature, than vapourisation of the carbon would be needed before reaction. The temperature required for this is about 4000K, which is hotter than temperatures achieved by flames.

A2 Energy Use

The reaction of coal may be given a thermodynamic basis by the use of several assumptions. The heating of coal to form hydrogen, methane, carbon dioxide, carbon monoxide and nitrogen in the gas phase, and carbon and ash in the solid phase, is a step with an endothermic enthalpy change of only about 80 J g^{-1} for a low rank coking coal (1), with reactants and products at 300K. For the present discussion this "heat of carbonisation" will be ignored, and also the gross thermodynamic properties of the char remaining from carbonization will be approximated to those of graphite. The reaction of coal to acetylene is then made equivalent to the reaction of a mass of graphite (given by the fixed carbon content of the coal) and a parallel reaction of the volatile gases of the coal. From a N.Z. non-coking coal containing 37 mass % volatile matter, about 50 mol % of the gases evolved

was hydrogen (2). The ultimate analysis gave an atomic ratio of carbon to hydrogen of about 1, equal to that of acetylene. Thus a high volatile coal may be able to supply sufficient hydrogen, allowing for recirculation of the latter, for acetylene as a single product. For the gases evolved from the N.Z. non-coking coal, methane, carbon dioxide and carbon monoxide contained over 95% of the "volatile carbon". Methane contained about a third of this, or little more than 10% of the total carbon in the coal. It can be seen that while methane is more accessible to reaction, it comprises only a small part of the coal as a raw material for acetylene production.

To estimate the energy use of coal for acetylene production, the reactions of methane and of graphite with hydrogen are compared below, with the understanding that the reaction of coal will be a combination of the two, more heavily weighted towards the graphite reaction. The comparison is also useful in that several arc processes use solely methane as a raw material, and are either economic or near economic (chapter 2). The minimum temperature to which the reactants can be taken to form acetylene is about 2000K. Both reactions are thus written for a temperature of 2000K:

$$2CH_4 \longrightarrow C_2H_2 + 3H_2 \qquad T = 2000K$$

$$2C_{graphite} + H_2 \longrightarrow C_2H_2 \qquad T = 2000K$$

In addition to supplying energy equal to the enthalpy change of these reactions at 2000K, energy must be supplied to raise the temperature of the reactants from room temperature to 2000K.

Thus the energy required is given by the reactions

$$2CH_{4\,T=298K} \longrightarrow C_2H_{2\,T=2000K} + 3H_{2\,T=2000K} \qquad \Delta H = 647 \text{ kJ}$$

$$2C_{graphite\,T=298K} + H_{2\,T=298K} \longrightarrow C_2H_{2\,T=2000K} \qquad \Delta H = 338 \text{ kJ}$$

The data used was taken from the JANAF thermochemical tables (3), and is given in appendix 2.

It is seen from the reactions that to produce the same quantity of acetylene, only 52% of the energy of the methane route is required for the graphite and hydrogen reaction. From this viewpoint, the use of coal to produce acetylene should require less energy than that required by the use of methane. In practice the most efficient plasmatrons require 9.0 kwh kg^{-1} acetylene from methane, whereas this analysis indicates 6.9 kwh kg^{-1} from methane, and 3.6 kwh kg^{-1}, or a little above, from coal.

There is a major drawback to this argument. A solid raised to high temperatures loses energy rapidly by radiation from its surface, at far higher rates than by radiation from a gas at the same temperature. To use a carbon material effectively as a raw material, it must be vaporised rapidly. A carbon surface brought to its sublimation temperature, roughly 4000K, radiates at 1.2 kw cm^{-2} of surface. In order to illustrate the effect of this radiation on the energy used, a one-dimensional model of an ablating carbon surface will be used. The carbon surface considered will be large enough to ignore edge effects.

The ablation rate, or the velocity at which the carbon face disappears can be seen to be the crucial factor. If the energy

advantage of the graphite route is just lost, or $(647-338)/2 = 154$ kJ mol^{-1} of carbon is radiated from the surface, then for a surface of 1 cm^2, $154/1.2 = 130S$ time is allowed for 1 mol of carbon to ablate through the area of 1 cm^2. One mole of carbon occupies approximately 5.5 cm^3 volume, so that the required velocity of ablation is $5.5/130 = 0.4$ mm s^{-1}. Ablation velocities larger than this would give the graphite route lower energy use than the methane route. It was toward achieving rapid ablation rates for graphite or coal surfaces that this project was therefore directed.

It is assumed of course in this working that the energy required to take carbon to its sublimation temperature and sublime it is reabsorbed in reaction to acetylene. With finite blocks of carbon material, radiation from the sides will become important, and may predominate with the ablation of small pieces.

3-B Energy Transfer to an Ablating Carbon Surface

A certain energy transfer to the carbon surface is required for it to ablate at a desired rate, and it appears that this must come from the gas phase. At the minimum ablation rate given above, the minimum energy transfer rate is calculated from the sum of that lost by radiation and that required by evaporation and heating the carbon. Evaporation and heating amount to $(280 + 55)$kJ mol^{-1} (see appendix 2), or $335/130 = 2.6$ kw cm^{-2}. Thus ignoring conduction losses, the minimum energy transfer at the carbon surface $= 1.2 + 2.6 = 3.8$ kw cm^{-2}. In order that the energy radiated be negligible compared with that used for ablating material, the ablation rate should be perhaps 5 times

the minimum i.e. 0.2 cm S^{-1}. This demands an energy transfer of 1.2 + 13 = 14 kw cm^{-2}.

To achieve this high energy transfer to a surface appears at first sight to be very difficult, at least if it is required to be efficiently done. 14 kw cm^{-2} corresponds to the power radiated from a black-body at 7000K. If radiation was to be the method of energy transfer, 14 kw cm^{-2} could be achieved by molecular radiators at high pressure at temperatures below 10,000K, or by atomic radiators at much higher temperatures. Both these situations appear costly to arrange. A method which would release the energy directly at the surface would be that using an exothermic chemical reaction at the surface, and this could perhaps be controlled by changing chemical potential gradients. The only species which can exist at a temperature of 4000K are simple molecules, atoms and electrons. Since reaction with hydrogen is required, a recombination of hydrogen atoms coming from a region hotter than 4000K is suggested as the reaction at the surface. However hydrogen is about 90% dissociated at 4000K, and this mechanism would be limited by the relatively slow diffusion of hydrogen molecules at a small surface concentration, from the surface back to the hotter region. Thus the surface at 4000K would be a poor competitor with other colder surfaces for the energy dissipates in the hot region, and the method again appears expensive.

A chemical reaction of the surface with electrons on the other hand, is simple to arrange, and the rate of reaction can be controlled by controlling the flow of electrons. The single

requirement here is that the surface and some of the solid behind the surface be electrically conductive, to carry away the electrons. This is no problem with graphite, but coal requires some processing, either by the conduction energy flow back into the solid, or previously to that, before a good electrical conductivity is obtained at lower temperatures. A suitable means of providing the high electron flux required at a surface, is an arc struck at that surface.

The enthalpy of electrons passing through an arc will now be considered. Since over 90% of the current of an arc is normally carried by electrons, and ions and electrons have about the same size of energy change, consideration of the electrons accounts for the most important initial energy dissipation in an arc. Electrons pass from cathode to anode through the arc, and it will be seen that the choice of anode for the ablating surface is appropriate. Choosing a common arc voltage for a carbon arc, 60V, the electrons in the cathode have 60 eV potential (or chemical) energy with respect to the anode. About 4 to 5 eV of this is lost as a work function term upon the electrons being emitted from the cathode, and a further loss of the order of 10 eV occurs upon the electrons entering the arc column proper. Gradual loss of the electron potential energy as the electrons pass through the arc then happens, until they arrive just in front of the anode with about 100 kJ mol^{-1} of kinetic energy and a much larger potential energy. With respect to a graphite anode, this last energy term consists of the work function of graphite (4.6 eV) together with the energy associated with the

anode fall, variously estimated at 20 and 30 eV for a carbon arc (see chapter 7). Taking this value as 20 eV, the total energy available for release in the anode amounts to 24 x 23 x 4.18 + 100 = 2300 + 100 = 2400 kJ mol^{-1} of electrons, a large amount compared to the normal chemical bond energy per mole. The current density required to dissipate 14 kw cm^{-2} can now be estimated. It is found to be 600 A cm^{-2}. By comparison, the current density for the "minimum" energy transfer given above is 115 A cm^{-2}. It can be seen that the energy dissipated for carbon vaporisation is but a third of the total energy dissipated in the arc. More will be written about this in the final chapter.

3-C Previous Work with Graphite and Coal Anodes

Previous workers attempting to react graphite and coal as anode material for acetylene production have appreciated that high currents ablate disproportionately larger amounts of carbon due to intensive heating at the anode, but have not considered radiation, nor have established any operating criteria for the more efficient use of energy in ablation.

C1 Graphite and Hydrogen

Work was reported in 1962 and 1964 (4,5) with a graphite anode in hydrogen which was carried out by Baddour and his students at Massachusetts Institute of Technology with a 25 kw reactor. A 6.3 mm diameter graphite rod was used as an anode, located centrally in a horizontal graphite tube of 12.5 mm internal diameter, which served as a cathode. Currents of up to 320 A, i.e. 970 A cm^{-2} on the anode, were used, resulting in anode

velocities of up to 10.5 mm s^{-1}. Voltages of approximately 50 volts were found, for a radial interelectrode distance of 3.1 mm. Hydrogen was brought in around the anode, through the arcing annulus formed between the anode and cathode. Gas samples were taken by quenching some of the flow through a water-cooled probe placed on the axis of the reactor, downstream from the arc. The sample flowed into an evacuated vessel. Sufficient anode length (300 mm) was used to obtain a 30 s run at the highest current. The length of run was also limited by the deposit of carbon about 20 mm downstream of the anode. After about 5 g of anode carbon had been used, (300 mm of rod) the cathode tube was usually "75% blocked" with deposit.

The results should be accepted with caution, for it has been seen with plasmatrons that sampling the fast-reacting mixture with a probe can give a composition correct along the axis, but nonrepresentative of the total flow. A conversion of 40% carbon from the anode to carbon in acetylene was found for concentrations of 13 mol % acetylene and a total pressure of reactants of 1 bar. For higher carbon to hydrogen ratios, concentrations of acetylene were as high as 25 mol %, with lower conversions. The minimum power requirement was roughly 300 kwh kg^{-1} acetylene formed. Several variables were investigated, and their influence on the reaction to acetylene are noted below for pointers to the design of a more efficient reactor.

Power Carbon ablation rate from the anode varied linearly with power. The rate was appreciable only when the current rose

above 60 A, i.e. 200 A cm^{-2}.

Hydrogen flow rate As the hydrogen flow increased, the carbon ablation rate fell somewhat, the concentration of acetylene in the product gas dropped, but the yield improved markedly (at the higher power levels).

Sampling Probe Size An optimum inside diameter of 1.5 mm was found for acetylene formation. As the sample was in choked flow through the probe, the interpretation given was that heat transfer rates were not sufficient on either side of the optimum. The reasoning followed was that the flow was too small with very small probes for cooling to occur rapidly, and the surface for a given flow decreased for the larger probe sizes, causing less rapid cooling. Quench times varied from 10^{-5} to 10^{-4} s. This investigation suggests that careful work on the effect of quench rates in more practical reactors may achieve better yields of acetylene. It is thought significant that Baddour's samples, giving higher concentrations than reported elsewhere, were reduced in pressure rapidly while being cooled.

Sampling Probe Position The probe was taken as close as 15 mm to the anode tip, and the highest acetylene concentration was found there. Acetylene concentration of the gas from the probe fell off as the probe was taken downstream. A distance of 110 mm, the maximum travel from the anode used, corresponded to a residence time of gases from the anode to the probe of about 4 ms (velocity of about 30 ms^{-1}), which is probably sufficient for appreciable decomposition of acetylene (chapter 2).

Hollow Anode The conversion to acetylene was significantly

improved by introducing the hydrogen flow through a hollow anode, from 20% to 50% for the same hydrogen flow and arc power. The latter was the highest conversion obtained.

Dilutents The addition of 20 mol % of helium to the hydrogen was sufficient to increase the acetylene concentration from 14 mol % for a 7.5 kw arc power and 18.6 mol % for a 10 kw arc power, to 23 mol % for both power values. Higher concentrations of helium (up to 60%), did not change the acetylene concentrations. Baddour interpreted the effect of helium to be equivalent to that of lowering the total pressure of reactants. According to his equilibrium calculations, the maximum amount of acetylene possible at a given pressure decreases with pressure. To explain his other results, Baddour turned to a consideration of kinetics of selected reactions. He proposed a scheme which according to him explains his high concentrations of acetylene, but according to his chart does not predict the large increase in acetylene concentration for a drop in total pressure from 1 to 0.8 bar that was observed with helium dilution. It seems that helium may act as a third body in an acetylene formation reaction, or prevent acetylene decomposition in some way.

Magnetic Rotation of Arc Initial work was done with the arc left to wander about the cathode tube wall. The second report describes work where an attempt was made to mix the reactants by rotating the arc about the anode. An axial magnetic field of about 70 gauss was generated by a current-carrying coil, and since the field was perpendicular to the electrode-electrode annulus gap, it was presumed that rotation of the arc occurred. When the magnetic field was applied, the voltage-current characteristic changed

from one where the voltage was independent of current, to one where a rise from 40 V at 150 A to 70 V at 300 A was observed. There was a cocurrent drop in anode erosion rate for a given power. For the same conditions otherwise, acetylene concentration was improved from 14 to 18 vol % by use of the magnetic field.

Methane The gas feed was changed from hydrogen to methane, for runs using solid anodes and a magnetically spun arc. Acetylene content in the quenched gas increased with arc power, and with overall carbon to hydrogen ratio. A very high value of 52 vol % acetylene was obtained. This suggests that the reactions of methane and the anode carbon with some of the resultant hydrogen may run independently, and that the reaction system is far from chemical equilibrium. The lowest specific energy requirement found was 66 kwh kg^{-1} acetylene, with 12 mol % acetylene concentration. The greatest conversion of carbon to carbon in acetylene was about 22%.

Ethylene was also found as a product, in concentrations of about 1 mol %. Baddour et al. state that this suggests a surface catalysed reaction from acetylene in the presence of relatively cool walls. The ethylene content did not vary significantly with change of probe size, suggesting also that the reaction occurred outside the probe, perhaps on the cold cathode walls.

C2 Coal

A report was published in 1964 (6) by workers at AVCO Corporation, Massachusetts, about an attempt to use coal as a consumable anode for acetylene production. In a batch experiment

lasting a minute, an arc was struck in vacuum between a 13 mm diameter cathode rod and an anode cup. The cup consisted of a 38 mm diameter graphite tube closed at the bottom, and filled with a mixture of 88 mass % high volatile bituminous coal and 11 mass % pitch. The latter was included presumably to bind the coal particles sufficiently long to allow them to fuse, and thus maintain a current path to the anode surface, before the particles exploded from the surface by the expansion of volatile matter. Gases from the coal filled the chamber, until the pressure rose to 1 bar, after which the pressure was kept constant by some release of gas.

Currents of 400 A were used, with arc voltages of 50-100V. Gas samples were taken from a position 10 or 20 mm above the anode surface by withdrawal through a water-cooled probe into an evacuated container. An acetylene composition of 5 mol % was obtained in the sampled gas, with 72 mol % hydrogen. The arc covered only a small part of the anode at any instant, so that most of the gases evolving from the surface did not contact the arc.

The AVCO workers described the advantages of working with a "high intensity" arc in a general way, but did not attempt to use the overall current densities on their anode which are normally required for the high intensity arc. Based on the entire cross-sectional area of the anode, they operated with a current density of 35 A cm^{-2}. From a photograph they show of a circular patch on the anode surface of 21 mm diameter which was hollowed out by the arc, one can estimate that the actual current density was at least 110 A cm^{-2}. The current density required on a graphite anode

before appreciable material loss occurs is about 100 A cm^{-2}. Since the coke which forms from the coal has a rapidly increasing electrical conductivity with temperature, the surface of the anode, should the arc attempt to wander, presents the most positive potential to the arc where it has the highest temperature, i.e. at the arc spot. For this reason, and because of the possibility that the electrical conductivity of the arc at the anode end depends upon material of low ionization potential issuing from the anode, the anode position would tend to remain steady, perhaps more so than with a graphite anode. Also the thermal conductivity of coke and coal is well below that of graphite at the same temperatures, so that the observation of an isolated region of arcing on a large coal anode surface, acting perhaps like a single graphite rod of similar dimensions, is not so surprising.

3-D Design

The problems of maintaining a carbon arc in an enclosed space include the build-up of solid carbon on cathodes, and keeping insulators around the electrodes from becoming conductors. Points required for the acetylene reaction include high current density on the anode, introduction of hydrogen is such a way that good mixing with the carbon is achieved, and probably very hot walls, to minimise decomposition and reduce energy losses. Problems associated with the coal feed were seen to be difficult ones, if coal was to be used as an anode. A column of pulverised coal would need to be supported up to the arc edge, with probable deterioration of the support, necessarily an insulator.

A fluidised feed of coal would largely bypass the efficient energy transfer from electron condensation. A solid rod of coal which could stand by itself for a short distance, and also conduct electricity, at least in the outside layers, would be most desirable. It was decided that to solve the arc-reaction practical problems, the coal feed problems would be ignored in the first experimental project, and the coal anode replaced by a graphite anode.

Emphasis was placed in design on the maintenance of high surface temperatures within the arc chamber, so that energy losses would be reduced by reradiation, and so that temperatures within the range for decomposition of acetylene (800-1600K) would not occur downstream of the reaction zone. In the author's knowledge, at least, this is a departure from other attempts at acetylene synthesis with arcs, where water-cooled copper surfaces have been used exclusively.

D1 Anode

The size of reactor will be dependent on the carbon feed rate, which in turn is fixed by the size of anode and its current density. The power supply available delivered a maximum current of 112 A. A diameter of graphite rods for anodes was chosen so that a current density of 100 A cm^{-2} (about that necessary for appreciable carbon ablation) corresponded to a current low in the available range. A diameter of 3.3 mm (1/8 inch) was chosen, which gave a current density of 100 A cm^{-2} for a current of 9 A, and a current density of 1150 A cm^{-2} for 100 A. At this higher current the carbon feed was calculated to be about 100g h^{-1}.

D2 Cathode/s

Several materials were considered for the cathode. Tungsten, pyrolytic graphite, and various forms of silicon carbide had suitable electrical conductivities. A high melting point or service temperature was needed, as well as a high thermal conductivity, so that control could be obtained over the cathode operating temperature. Some properties are presented below.

Material Property	Pyrolytic Graphite	Self-bonded Silicon Carbide	Tungsten
Melting temperature T/K	4000 (Sublimation)	3100	3680
Electrical Resistivity, R/Ω m	2×10^{-6} C axis	10^{-3} to 10^{2}	5×10^{-9}
Thermal Conductivity, $k/Jm^{-1}s^{-1}K^{-1}$	280 C axis	40 to 280 at 1300K 150 at 1700K	200

All values are at room temperature unless stated otherwise. The silicon carbide, although more easily fabricated than the other materials, was rejected because of its lower melting temperature. Pyrolytic graphite has several advantages such as good insulation, both electrical and thermal, across the C face, as well as resistance to chemical attack on this face. Thus a cathode made of this material would presumably act as cathode only where the edge

of the layer planes were exposed. The difficulty of making or obtaining samples as large and long as was needed, precluded this material from the list. Tungsten was chosen, even though tungsten carbide is formed with carbon, with the hope that a very hot cathode would have little carbon reaction.

With the assumptions that thorium doped tungsten was available, and that the thermal emission mechanism operated at the cathode, the electron emission density at 2100K is known to be 3.4 A cm^{-2}. Cathode area was thus about 30 cm^{2}. Above 2200K, the thorium is rapidly vapourised, and the electron emission drops to that for pure tungsten, which climbs again to the same current density at a temperature of 2800K. In order that the cathode terminal of the arc be manageable in size, the surface area was reduced by raising the allowed operating temperature. At the m.p. of tungsten, a thermal electron emission of 445 cm^{-2} was calculated. Since this emission can be increased by field emission due to the cathode voltage drop but only to the extent of about 50%, according to the Schottky equation (7), then the operating current density was limited to 450 A cm^{-2}. The mechanism of electron emission from cathodes in arcs is not well understood, for current densities far exceeding these have been observed on cold cathodes. See, for instance, reference (7). The positive ion contribution to the current was expected to be less than 10%. From the above, the current density of 450 A cm^{-2} is a conservative estimate, giving a cathode tip area of 0.22 cm^{2}.

The anode-cathode configuration was chosen so that the stream of material from the anode was directed in a straight line

towards the outlet. Inadvertent recycle within the reactor could cause acetylene decomposition, perhaps reaction to ethylene, and certainly problems of wall erosion. It is common for a magnetic pumping action to occur at a cathode, producing axial velocities of the gas away from the cathode of several hundred metres per second. The direction of this "cathode jet" could not oppose the anode stream for the reasons given above, but yet was required to impinge on the anode stream for arc stability and for good mixing. A solution suggested by the work of Amman et al.(6) was the use of a cathode ring, but the problems of fabricating tungsten to this shape prohibited it. The design that was chosen was that of three cathodes, equally spaced around a circle concentric with, and at right angles to the anode. Tungsten rods which were readily available could be used, and mixing could be obtained with axial symmetry of flow, provided that the current was distributed evenly to each cathode. The cathode cross sectional area calculated above corresponded to three 3.3 mm (1/8 inch) diameter cathodes.

D3 Insulator

A critical component was the electrical insulator around the anode. This was required to prevent the arc from wandering from the anode, and had to withstand high radiation fluxes from the arc and anode. Materials considered were fully dense alumina, vitreous carbon, pyrolytic graphite (across the layers), silicon nitride, and hot-pressed boron nitride. Despite some attractive properties, the first three were eliminated because

of difficulty of fabricating complex shapes. Silicon nitride has a specific electrical conductivity of $5 \times 10^{-2} \Omega^{-1}$ m^{-1} at 1300K, a thermal conductivity of 1/3 that of graphite at this temperature, and a melting point of 2100K. Boron nitride has a lower electrical conductivity, i.e. $3 \times 10^{-3} \Omega^{-1}$ m^{-1} at 1300K, and $1.7 \times 10^{-1} \Omega^{-1}$ m^{-1} at 1800K. It has a thermal conductivity about half that of graphite at 1300K, and has a high decomposition temperature of 3270K. In the hot-pressed form considered above, it has a graphite structure, so that it can be machined very easily. Boron nitride was chosen as the insulator material.

D4 Reactor Chamber

The details of the surrounding walls were considered. Consistent with the aim to keep the walls hot, graphite was chosen as the wall material. Although electrically conducting walls could be a nuisance, some continuous deposit of carbon on any substrate would effectively give a graphite surface, rendering choices other than graphite superfluous. Graphite is easily shaped, and no further chemical elements are then introduced into the system. Hydrogen was brought in, in three flows, one to each cathode, as shown in figure 3.1. The reason for its introduction at the cathode was that it would be inducted into each cathode jet, and well mixed with the carbon from the anode.

For an atomic ratio of hydrogen to carbon of 5, and a current of 100 A, the gas issuing from the reactor was calculated to have a volume rate of about 10^{-3} m^3 s^{-1} at 4000K. A 6.6 mm (1/4 inch) diameter exit was chosen, with a resultant exit

SCALE: FULL SIZE

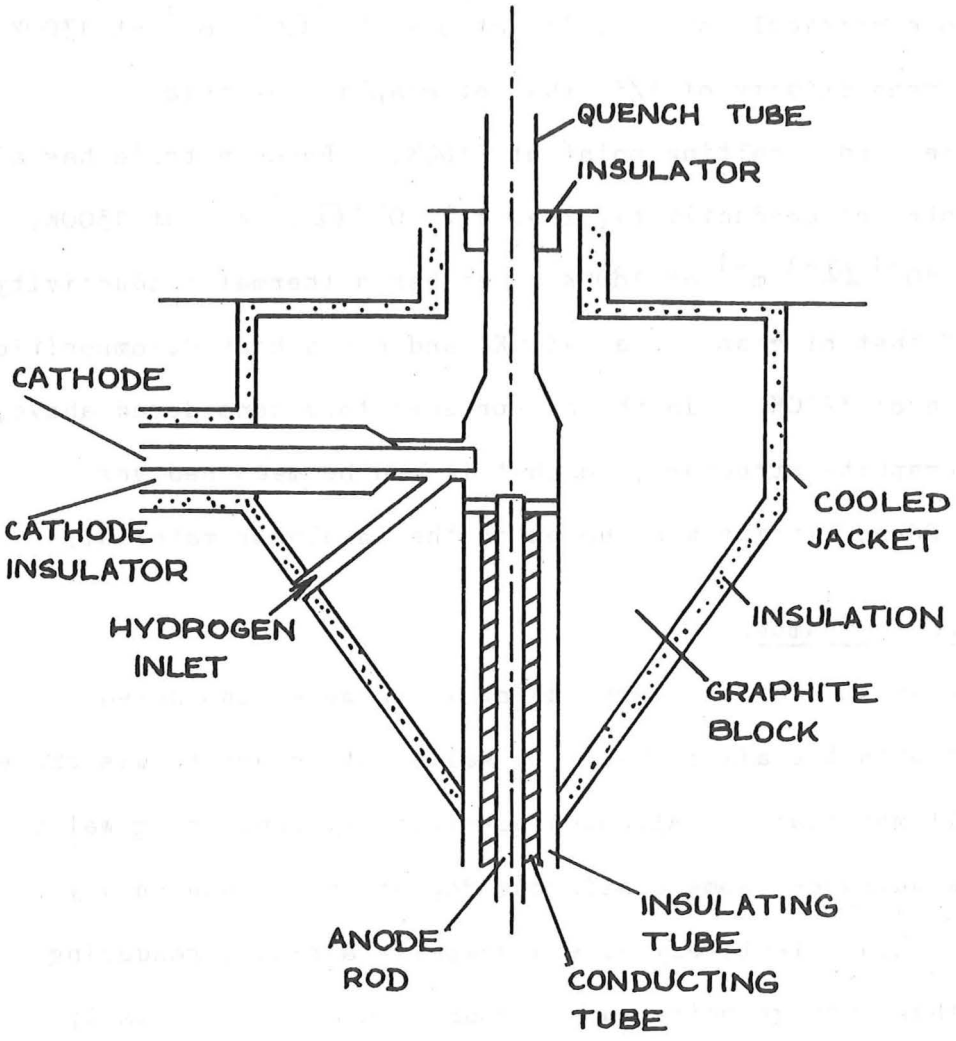

FIGURE 3.1 ELEMENTS OF THE REACTOR DESIGN

velocity of about 50 m s^{-1}. If the carbon came off the anode as C_2 it was calculated that the stream velocity in front of the anode due to expansion was about 50 m s^{-1}, with perhaps about the same contribution from a lateral body force on the charged particles from the self magnetic field of an arc contraction at the anode. Thus a rough estimate of reaction time before the quench tube was L/500 seconds, where L was the distance from mixing of the reactants to the beginning of the quench tube in mm. For a reaction time of 1 ms, this distance was thus about 50 mm. The reactor body was proportioned so that this characteristic length was used.

The resistive heating through anode and cathodes was checked, and found to be small (0.2V drop along anode and tube). Detailed heat transfer calculations were carried out on the cathode and its boron nitride cover. The wall thickness of both the graphite anode tube, which provided an electrical contact with the anode rod, and the boron nitride insulating tube were limited to 2.5 mm by the purchase of 13.3 mm outside diameter boron nitride, an economic size. The length of anode tubes was then determined from the heat transfer considerations to be 40 or 50 mm in order to keep the boron nitride insulator below its decomposition temperature. An energy balance was made over the cathode surface involving electron "evaporation" energies, radiation, positive ion energies and conduction back along the cathode, but unfortunately ignoring the convection heat transfer to the hydrogen. On this basis, the length of cathode was found to be 40 mm for a temperature of 3650K at the tip, and water cooling at the end.

As the lengths of both anode and cathodes beyond where water cooling was applied, were determined, the size of the graphite block was largely fixed. To reduce energy loss from the graphite block, and also to make the entry of an angled hydrogen feed easy, the anode end of the block was conical. It was apparent that with a temperature of 300K at the outer surface of the graphite block, the inner surface would be at much too low a temperature. A disadvantage in providing a gap between the block and a water cooled metal surface was the difficulty in preventing circulation of arc chamber gas around the gap, causing ambiguous reaction results and perhaps the breakdown of electrical insulation. It was decided to use magnesium oxide powder with a melting temperature of 3100K for insulation between the graphite block and a cold copper wall. Using an estimate (220 W) of the radiation loss to the inner graphite wall and setting the latter at 2500K, the outer temperature of the block was 2000K, with 1700K drop in temperature over 3 mm thickness of powder. With this arrangement, it was calculated that about 5 minutes were required for steady state from start-up. This design was based on a current of 100 A and voltage of 45 V.

D5 Reactor Shell and Fittings

A double copper jacket was constructed as shown in figure 3.2, with the space between the copper sheets provided for circulation of cooling water. To ensure positive circulation, water was brought in at three points, one on each cathode assembly, and taken out at one point near the anode flange. Ports for hydrogen entry, and for

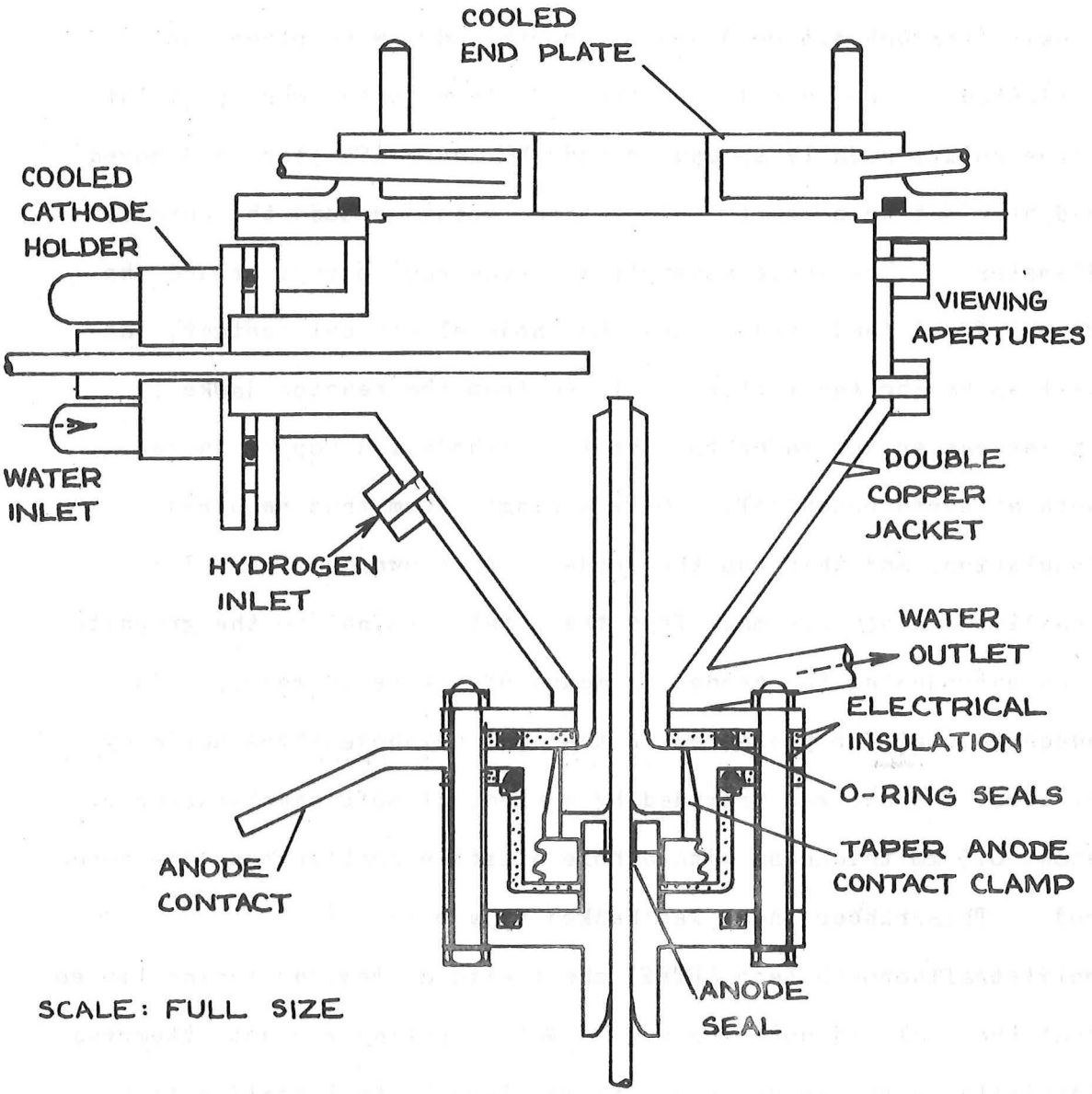

FIGURE 3.2 REACTOR SHELL, END PLATE, AND CATHODE AND ANODE ASSEMBLIES

viewing through 3.3 mm diameter quartz rods, were placed as indicated. For cooling of the end plate, water was fed in at three points equally spaced around the inner diameter, and moved radially out to be collected at three points around the outside diameter. The anode assembly was required to seal around the graphite rod feed, and around the anode electrical contact, as well as having the latter insulated from the reactor jacket. It was easier and safer to make the cathode and copper jacket both at earth potential. Only a single item thus required insulation, and this was the anode. As shown in figure 3.2, a positive contact was made from the metal terminal to the graphite bush surrounding the anode, by means of a tapered wedge. An adequate seal for pressures in the reactor above atmospheric by at least 0.6 bar was provided by a piece of soft sheet-rubber of about 0.5 mm thickness with a hole a little smaller than the anode rod. This rubber sheet was backed by a piece of polytetrafluoroethylene (PTFE) sheet with an inwards facing lip so that the seal did not blow out. Water cooling was not attempted initially on the anode, since it was thought that cooling from the reactor walls was sufficient.

D6 Anode Feed

A prime requirement for the carbon feed was that it be continuous for at least 5 minutes. Graphite was available in 0.3 m lengths, so that five to ten lengths were needed to be fed end-to-end for a high current run. A magazine was devised to hold about twenty rods, and to bring each rod in turn in contact

with two wheels, one of which was rubber. The rubber wheel was spring-loaded towards the other, and driven through a flexible drive by a 40 watt D.C. motor. The speed of the motor was easily controlled through a wide range with high torque by providing a constant voltage of 50 volts through a rectifier to the field coil, and a varying voltage from 0 to 50 volts through a variable transformer and separate rectifier bridge to the armature. Each anode rod was connected to the following rod by machining a spigot on one, and a hole to fit, in the other.

D7 Hot Gas Quench

The simplest device used in the past for cooling the hot gases from the reactor was a cooled tube through which the gases passed. Alternatives included a liquid spray quench, a fluidised bed, or cold gas mixing. The simple tube had the advantage that dry product gas could be sampled for analysis without further treatment other than removal of soot, and no correction needed to be applied for estimation of true concentrations. A series of three quench tubes of 15, 30, 50 and 70 mm in length, each 6.6 mm inside diameter (1/4 inch), were constructed, so that the quench tube length could be varied from 15 mm to 165 mm. As shown in figure 3.3, the partially cooled gas was then brought into a larger chamber of 31 mm inside diameter and 200 mm in length, for further cooling to room temperature. Following the practice of Baddour, a cooled probe was placed axially within this chamber, through which samples could be withdrawn. Samples were also to be taken downstream of the cooling chamber.

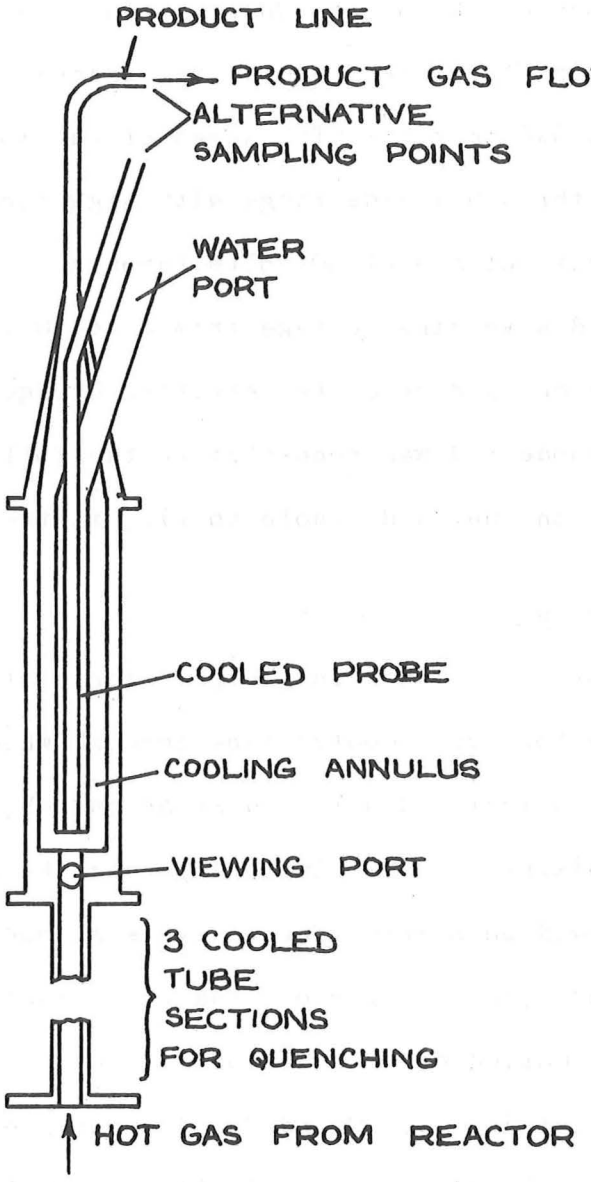

FIGURE 3.3 QUENCH TUBES, COOLER AND SAMPLING PROBE

The length of quench tube required was calculated using an empirical relationship established for plasma stream cooling (8), relating the enthalpy of the gas to the position in a pipe. In this instance, the enthalpy dropped to 0.1 of its initial value in 90 mm length of tube with a cooling time of about 2 ms.

In order that energy losses to the reactor were found separately from the heat transfer to the quench tube, a thin sheet of PTFE sheet was esimated to be sufficient insulation when placed between the reactor-quench tube flanges. (Only about 5% of the reactor shell heat transfer was estimated to pass to the quench tube with no insulator.) Similar insulation was placed between the quench tube and cooler.

A further observation port was planned so that observations could be made right through the quench tube almost at the end of the quench operation. The quench tube walls were made from copper, but copper was avoided in the cooler, where the product gases were colder, because of the catalytic action of copper acetylide on the explosive decomposition of acetylene. The inside surfaces of the cooler were constructed of stainless steel.

D8 Power Supply

The direct current supply was available with a voltage of 250 V, and currents up to 110 A. An adjustment of supply voltage to the arc voltage (from 40 to 100 volts) was made by using a resistor in series with the arc. This had the advantage of giving stability to the arc, although being very

wasteful of power. Up to 20 kW was needed to be dissipated in the ballast resistor, for 4 to 8 kW in the arc. The ballast resistor was made up of thirty 1 kW bar radiator elements arranged in 5 tiers of 6 elements in a vertical chute. Sufficient air flow was provided over the elements to carry away 20 kW with a temperature rise of only 50 K. All the elements were in parallel, with a single switch on each of 4 tiers, and a switch on each element of the 5th tier. By switching in more resistors, the current could be increased in steps of 2.5 A from 0 to 100 A.

The rectifier in the D.C. power supply rectified half wave, so that a ripple of 150 Hz was obtained superimposed on the direct current. This ripple was observed as 48V A.C., i.e. a proportion of 19% of the D.C. voltage. Since this was likely to complicate the chemistry of the reactor, and since photo-electric measurements were planned on the arc, an inductance load was placed in series with the arc. It was calculated that an inductance of 0.3 Henries was needed to reduce the ripple to 0.9%, a figure acceptable for optical measurements (9). This was provided only in small part by an air core inductance with 100 turns at a radius of 30 cm, which reduced the ripple to 45V r.m.s.

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EXPERIMENTAL

CHAPTER 4

Contents

Materials - graphite. hydrogen.

Apparatus - mass flows. sampling. electrical. water. chromatograph. spectrograph. radiation standard.

Procedure - preparation for run. run. analysis.

Sufficient measurements were made so that all mass flows and concentrations were known, and so that some check could be made on accuracy. Measurements were made of energy flows both in and out of the reactor, and an energy balance attempted. The values of process parameters were noted at frequent intervals throughout a run, in an attempt to completely characterise the run conditions. Additional observations such as those using a spectrograph were made from time to time.

4-A Materials

Graphite - Union Carbide graphite, grade CS 3.3 mm diameter in 300 mm lengths. Maximum ash content 0.1 mass %.

Hydrogen - > 99.7 mol % hydrogen on dry basis

< 0.01 mol % oxygen

< 0.01 mol % nitrogen

< 0.01 mol % carbon dioxide

$< 5 \times 10^{-6}$ mole fraction carbon monoxide

$< 10^{-5}$ mole fraction other carbon compounds

moisture varied from 0.02 to 0.14 mol %

4-B Apparatus

An outline of the experimental set-up is shown in figure 4.1.

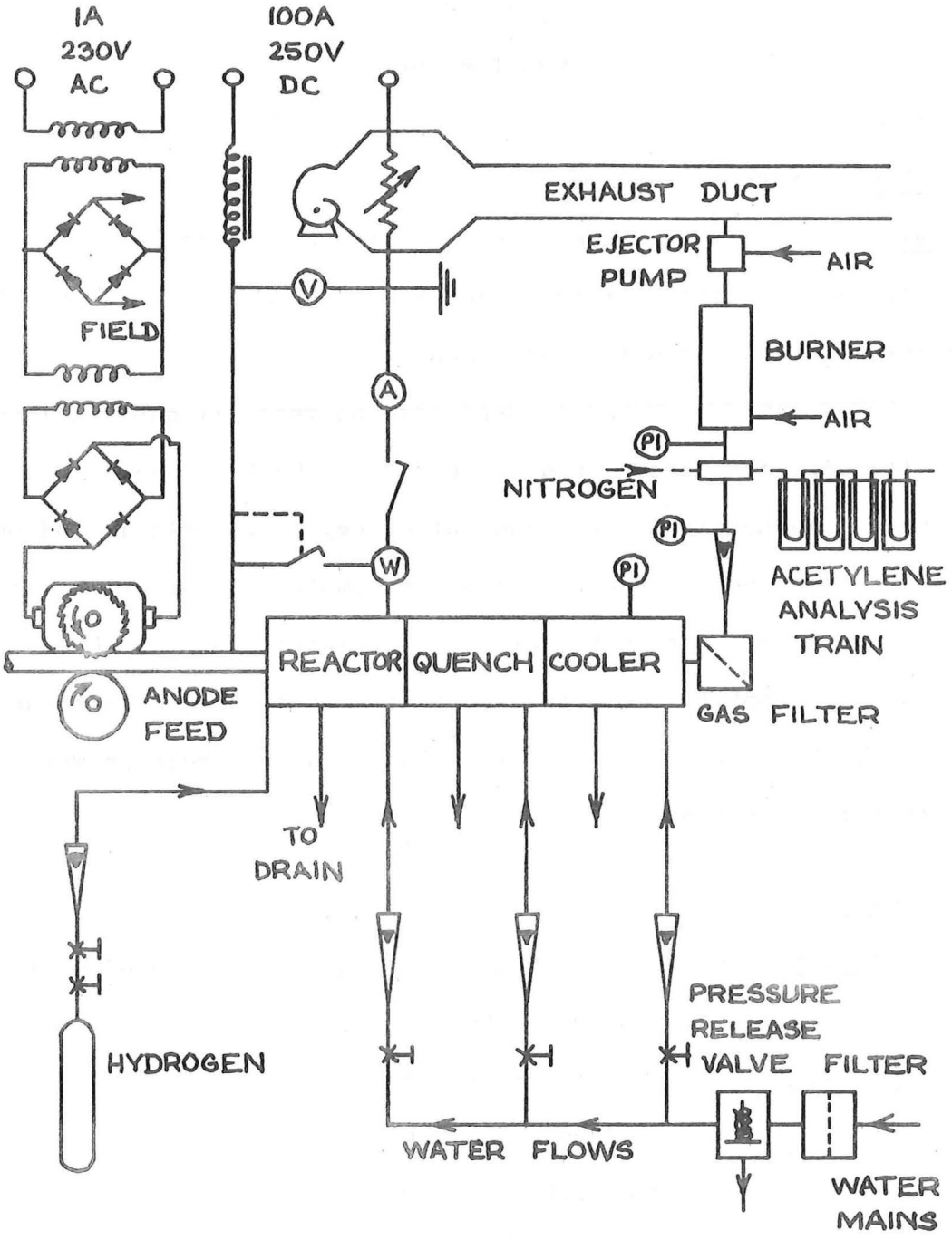


FIGURE 4.1 LINE DIAGRAM OF REACTOR FLOWS

Hydrogen was fed from a pressurised bottle through a pressure reducing valve, a needle valve, and a Fischer and Porter 1/4" low flow rotameter to the reactor. This rotameter was calibrated for hydrogen flow under the pressure used in the runs, (0-0.07 bar above atmospheric) as were other hydrogen rotameters, by liquid displacement rates in a measuring cylinder. Carbon feed velocity was gauged from the variable transformer setting, which was calibrated and checked several times during the course of experiments. From the velocity, with the assumptions that anodes were a constant cross section, and constant density, the mass feed rate of carbon was calculated.

After filtering the carbon off, the product gas passed through a rotameter. It was then sampled for acetylene analysis, and burnt to remove some possible traces of hydrogen cyanide. An air ejector then pumped the products of combustion into the duct which ran from the resistor banks to outside the building. The product gas rotameter was calibrated for both hydrogen and acetylene, and an interpolation was made between these calibrations for acetylene concentrations in hydrogen of less than 100%. An eight port push-pull valve was constructed to transfer a loop of product gas to a carrier gas stream of nitrogen which bubbled through a series of four 20 ml test tubes for chemical analysis of acetylene according to ASTM D1020-61 (1). This standard method analyses for monoalkyl acetylenes and diacetylene, but not dialkyl acetylenes. Successive test tubes were filled accordingly with dilute sulphuric acid to remove basic compounds, with sodium metasulphite solution to remove carbonyl compounds,

with sodium hydroxide solution to remove acidic compounds, and the last one with an alcoholic solution of silver nitrate to form a silver acetylide precipitate. The acetylide reaction forms acid, which was titrated with a standard solution of sodium hydroxide to determine the acetylene in the sample taken. Each sample occupied exactly the same volume at product line pressure, which was kept constant at atmospheric pressure by the control of the air ejector so that a mercury manometer open to atmosphere had a zero differential head. The nitrogen used as carrier gas was 99.9% pure on a dry basis, and distilled water was used throughout. The sampling valve, and a flow distributor are shown in figure 4.2.

Measurements of arc voltage were made with a new Avometer Mk5, and measurements of current with an industrial type 5 mV voltmeter and shunt. It was found that arc voltages and currents fluctuated more than was acceptable for an estimate of arc power. A Weston wattmeter was installed, and power readings were found steady and reproducible. As the voltage coil of the wattmeter was designed for a 0-110V range, it was connected only when the arc was operating, by means of a relay switch actuated by a potential difference across the ballast resistor.

Mains water delivered between 3.5 and 5.5 bar gauge was used for cooling. It was filtered to avoid build-up of grit in the reactor cooling channels, and passed through a pressure relief valve which maintained a steady pressure to the cooling circuits. Three water flows were used, each with a needle valve and rotameter. The rotameters were calibrated at a point near their full range, and these calibrated flows were used thereafter in all runs.

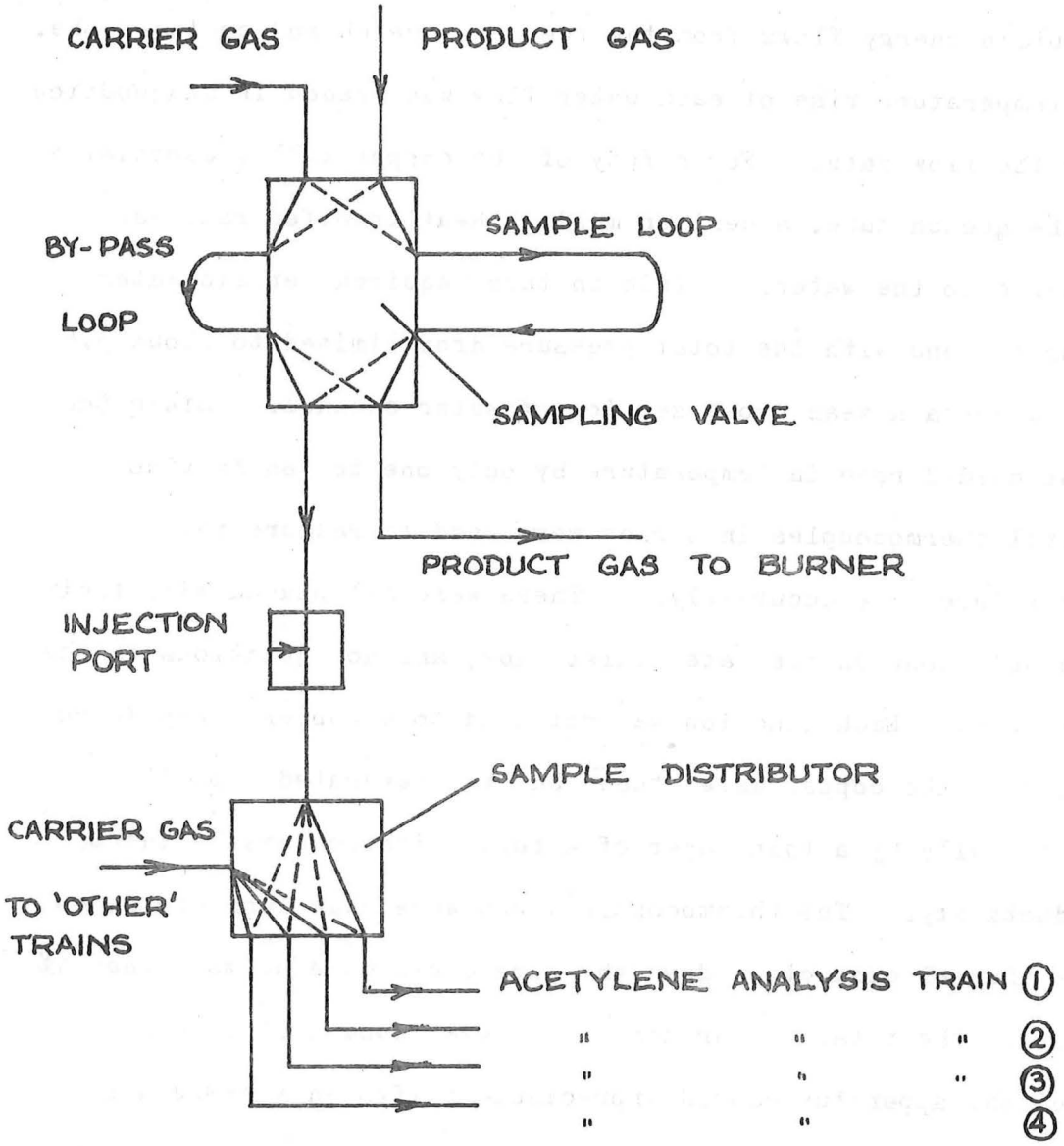


FIGURE 4.2 GAS SAMPLING VALVE AND DISTRIBUTOR

To obtain energy flows from the reactor, quench and cooler-probe, the temperature rise of each water flow was needed in conjunction with the flow rate. For safety of the copper walls, especially in the quench tube, a certain minimum heat transfer rate was required to the water. This in turn required certain water velocity, and with the total pressure drop limited to about 3.5 bar, a certain mean cross-section of water channel. Since the flows needed rose in temperature by only one to ten Kelvins, several thermocouples in series were used to measure this temperature rise accurately. These were all placed with their cold junctions on the water inlet tube, and hot junctions on the exit tube. Each junction was soldered to a copper strip which encircle the copper water tube, but was separated from it electrically by a thin layer of a resin with reasonable thermal conductivity. The thermocouple wires were made long enough so that thermal conduction down the wire could make no more than 1% error in the total measurement. It was found that draughts about the apparatus caused appreciable drifts in thermocouple readings, so all thermocouple junctions were packed round with cotton wool, and junctions and wire bundles enclosed with a plastic envelope. This eliminated observable drift. Thermocouple e.m.f. values were recorded continuously on strip chart recorders. Hitachi 2 pen and 1 pen recorders were used, because their amplifiers were guarded well against the influence of external magnetic fields, and because of their floating earth.

The thermocouple arrangements were each calibrated in situ by replacing the reactor with a water heater. The heater consisted

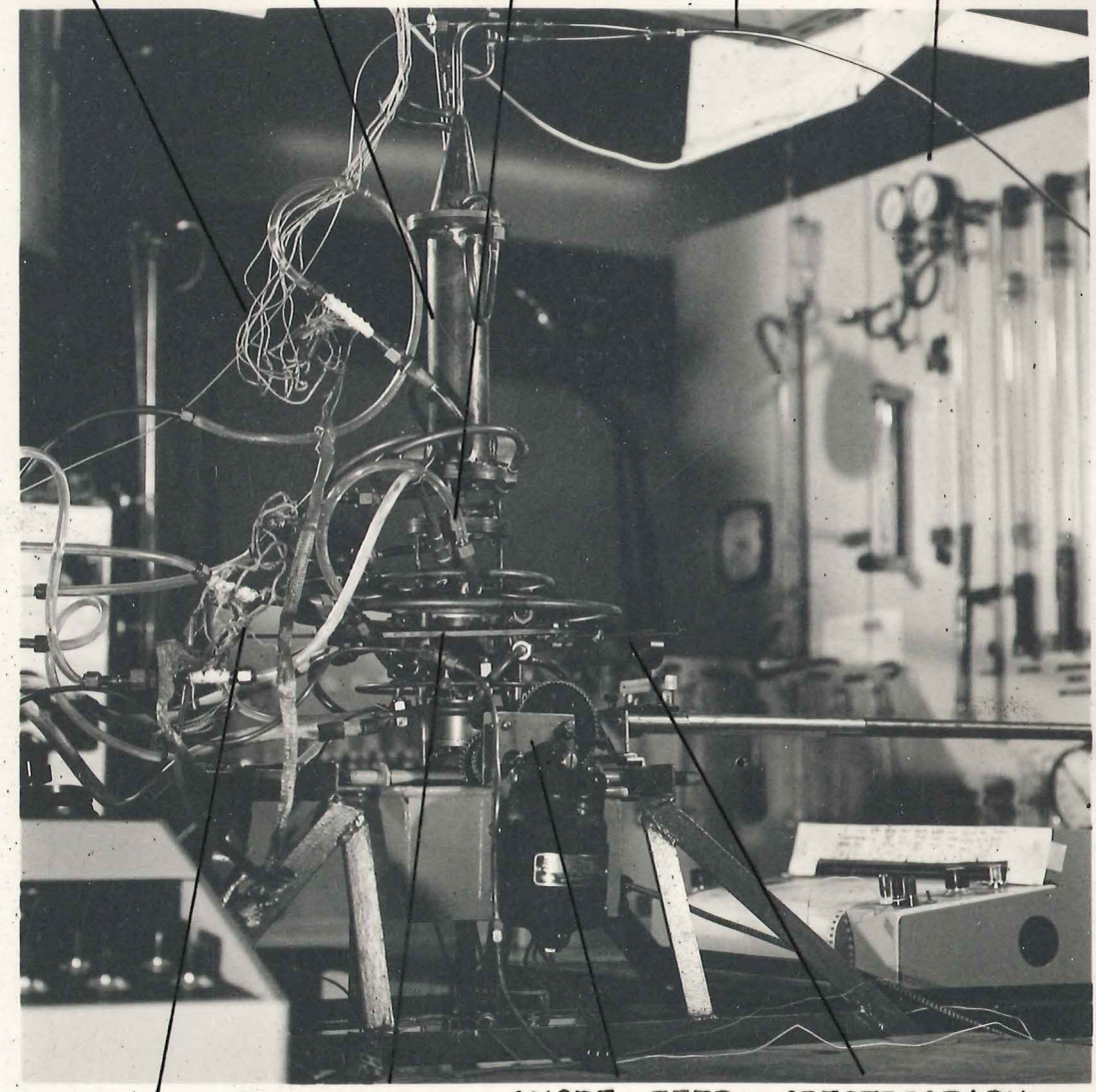


PLATE 4.1 ARC REACTOR ASSEMBLY

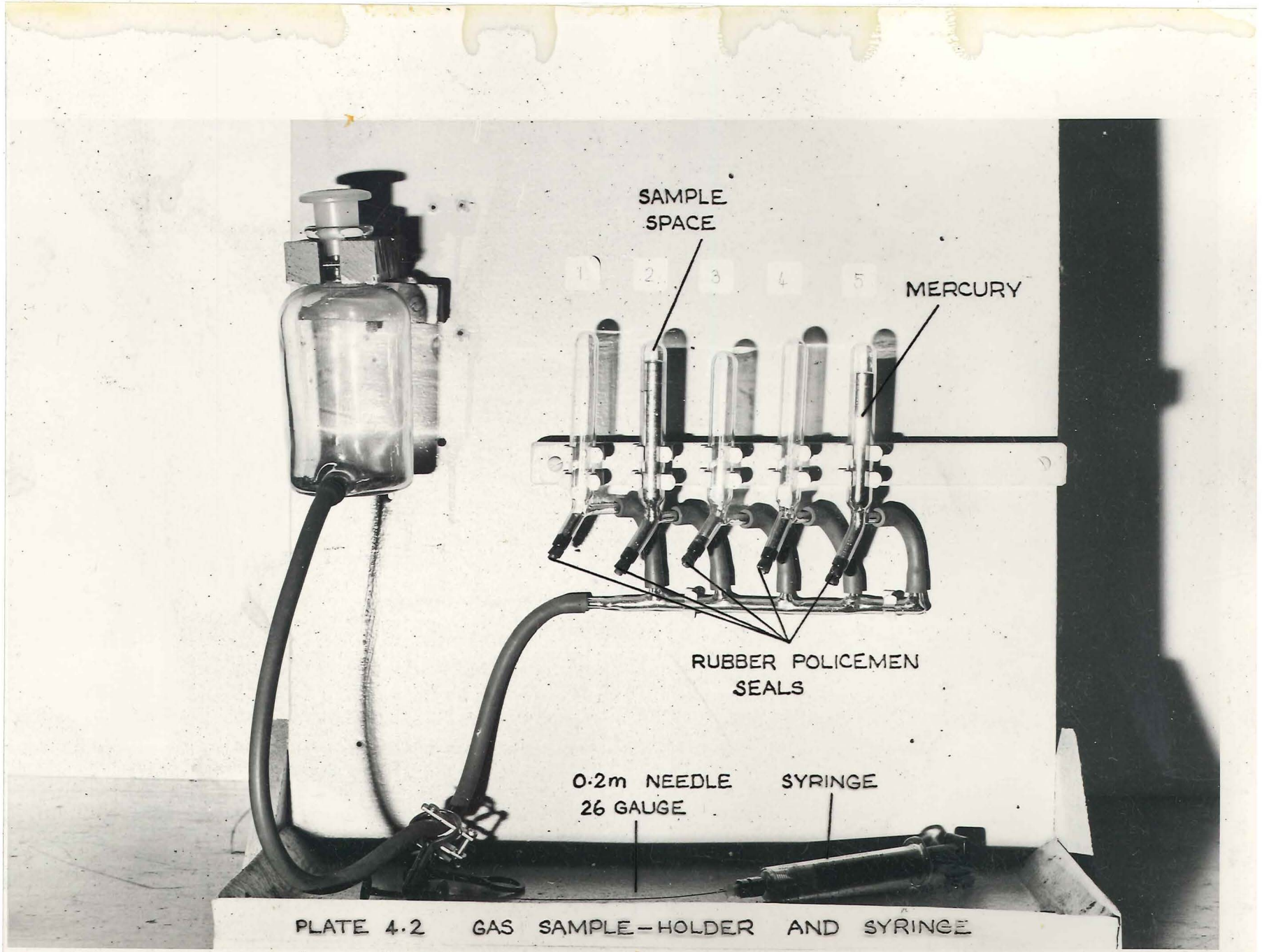


PLATE 4.2 GAS SAMPLE-HOLDER AND SYRINGE

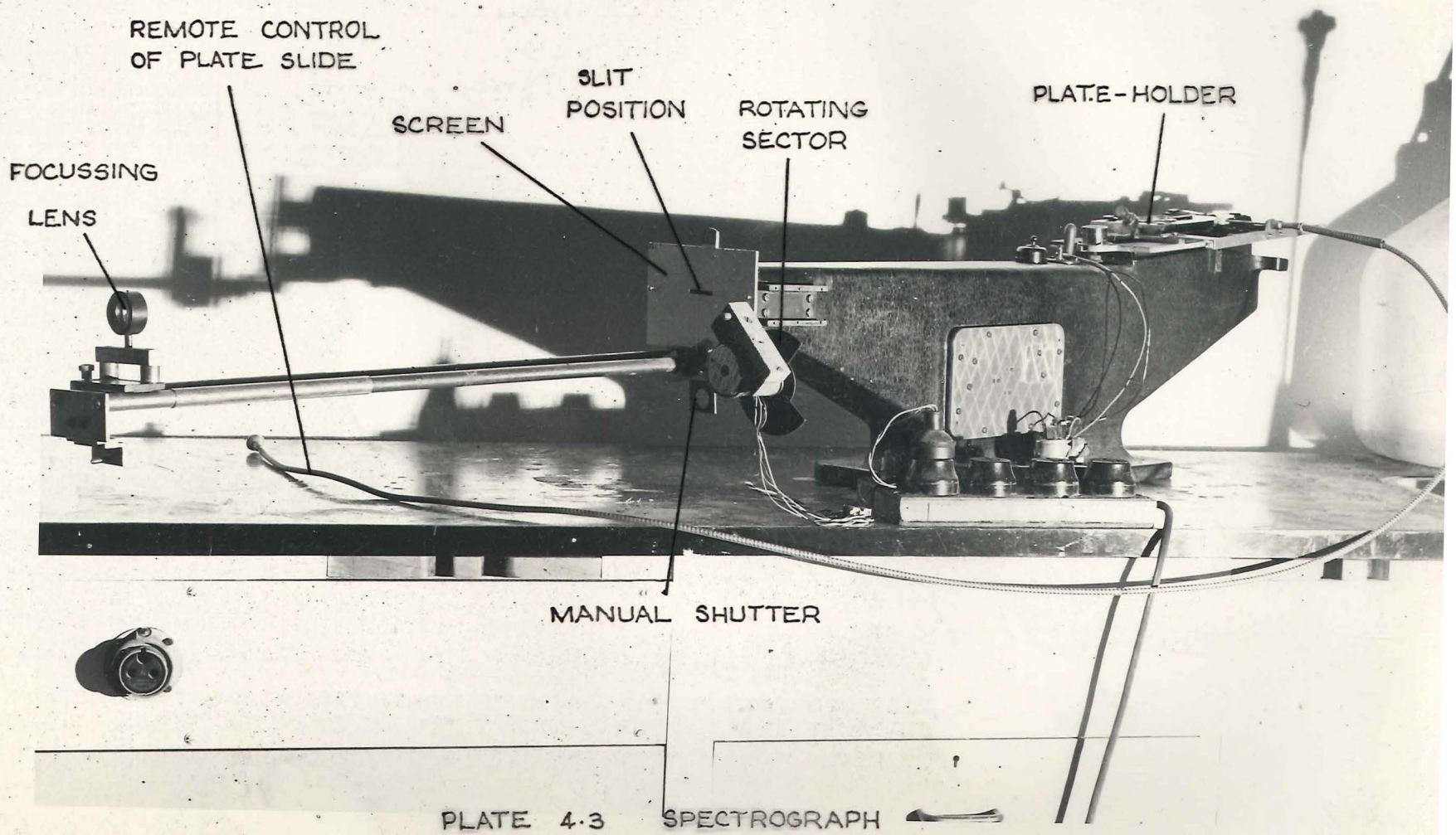

REMOTE CONTROL
OF PLATE SLIDE
SCREEN
SLIT
POSITION
ROTATING
SECTOR
PLATE-HOLDER
FOCUSSING
LENS
MANUAL SHUTTER
SPECTROGRAPH

PLATE 4·3

of a sealed, thermally insulated tin in which was placed a jug element connected to the D.C. supply. For different power dissipation levels, measured by the wattmeter, different readings were obtained from the strip chart recorders, making up a direct calibration. The standardised water flows for each cooling circuit were used.

All valves were arranged handily either in a row at bench level, or on the control panel, as shown in Plate 4.1. Almost all pressure and flow indicators were arranged on the panel. An isolating switch for the full current rating of the supply, was located on the bench in easy reach. Elephant trunking connected to an air extraction system was placed with its end about 0.1 m from the reactor, to carry away fumes if the seals leaked.

Gas samples were also taken from the product line by a syringe, the needle of which was inserted through rubber septa set in the line. Hamilton "gas-tight" syringes with a PTFE barrel head were used to transfer the samples from the line to a sample holder, shown in Plate 4.2. The gas displaced mercury, which then sealed sufficiently well to allow no observable change in composition of a mixture of hydrogen and acetylene over a period of a month. The seals through which the syringe needle passed were rubber policemen pushed into the glass tube against the mercury head. Small brass guides for the needle were then placed inside the rubber policemen.

The gas samples were transferred from the holder to a gas chromatograph at leisure, for analysis. This again was done with the Hamilton syringes. Two columns were made up for the gas

chromatograph by G.Sutton (2), according to some column specifications obtained from CSIRO, Sydney.

The specifications were:-

(a) for separation of permanent gases

1.4 m x 1.8 mm i.d. stainless steel tubing containing 25% squalane on 60-85 mesh acid washed Chromosorb P, held at about 30°C, followed by 2 m x 1.8 mm i.d. stainless steel tubing containing 60-85 mesh 5A molecular sieve held at 85°C.

(b) for separation of hydrocarbon gases

14.0 m x 1.8 mm i.d. stainless steel tubing containing 25% propylene carbonate on 44-52 mesh Chromosorb P (not acid washed) followed by

1.4 m x 1.8 mm i.d. stainless steel tubing containing 25% tetraisobutylene on 52-60 mesh acid washed Chromosorb P, both columns held at about 30°C.

The 5A molecular sieve available was 40-60 mesh size, and the Chromosorb P, both acid washed and unwashed, was available in the sizes 60-80 mesh. These sizes were used. The above specification noted helium as the carrier gas, but oxygen was used, as a paramagnetic oxygen analyser was used as the detector, as conceived by J.B.Stott. The two column trains were placed in parallel, with a push-pull valve enabling one to divert the carrier stream and sample to either column train, while still flowing out to the same detector. A problem was found with the long hydrocarbon separating column, in that a high pressure of at least

2.7 bar was required for a reasonable flow. It was found that the syringes were not gas-tight at this pressure, and indeed it was very difficult to inject a sample against this pressure because of the force required on the barrel. This difficulty was surmounted by using yet another push-pull valve with 8 ports. A loop of carrier gas was isolated with the valve, and the pressure in the loop reduced to 1 bar by expansion. The sample was then injected easily, the pressure increased to the previous value by contraction, and by moving the valve barrel the loop was swept into the carrier stream. Expansion and contraction was accomplished by a retractable piston, which was given a good seal by being covered with mercury. Mercury also covered the septum required for injection. For good measure, mercury was also kept above the barrel of the syringe, to guard against leakage of the gas sample.

Occasional observations were made with a medium-quartz Bellingham and Stanley spectrograph, of 1937 vintage. The light emission from the arc and anode which passed through a small quartz window was focussed on the slit of the spectrograph by a quartz lens. The image of the slit was then broken into a spectrum by the Cornu type quartz prism, and focussed on to the position of the photographic emulsion, over all its length, by a further quartz lens. Unfortunately, when the spectrograph was obtained, the slit was noticeably worn in the centre, and the image was focussed only at the red end of the range. Both jaws of the slit were taken out, honed down to a sharp edge so that no reflection could be seen edge-on under a low power microscope, and adjusted

for both edges closing in the same plane, and for touching at all points along the edges at the same time. The scale on the opening mechanism was then calibrated with the opening of the slit, as measured under a travelling microscope. The spectrograph was systematically focussed by rocking the photographic plate holder about its central pivot by short increments, and varying the focussing lens position over its full range for each position of the plate. Sensing the focus could not be done by eye, for the eye is restricted to about 1/4 of the spectral range. An exposure had to be made using spectral lines both in the red and in the UV on the photographic emulsion, and this developed, for one to know whether the lines were sharp throughout the spectrum. A combination of a carbon arc, which gave the atomic carbon (CI) line at 258 nm, and a sodium lamp, which gave the sodium D lines at 589 nm, was found to be excellent.

The dispersion of the spectrograph in the red was about 4 nm mm^{-1}, and greater for shorter wavelengths. Thus the sodium D lines were not resolved (0.6 nm separation) for any slit width. Extensive background exposure was found on the exposures. This was almost eliminated by cleaning the optical surfaces, thus reducing scatter, and by sealing round the plateholder with black tape, which prevented light leakage from outside the spectrograph. Unfortunately scratches were observed on the focussing lens, and also the optical path did not remain in a vertical plane perpendicular to the slit.

A carbon arc radiation standard was developed for calibrating the photographic emulsion on each plate.

The carbon arc standard consisted of a horizontal anode, 8 mm in diameter, made from grade CS National Carbide graphite, and a vertically placed cathode, 3.3 mm in diameter, of the same material. An arc was struck in air between the electrodes, and operated so that the cathode was 5 mm in front of the anode face, and 5 mm below it. The radiation from the anode face was focussed on the spectrograph slit, and used as a light source radiating as a black body at 3800 K as determined by Hattenburg (3). The maximum current used without the anode attachment of the arc contracting and wandering over the surface, was 13 A. Unfortunately the device could not be operated with the current continuously adjustable, and so just below the unstable condition, as desired for most accurate work. The current was adjustable in steps of 2.5 A, and so would be within 80% of the maximum value for the "quiet mode". For the accuracy possible with the spectrograph, this should have given sufficiently accurate calibrations. So that similar optical paths were used in taking spectrographs of both the reactor arc and the calibration anode, the same quartz window was used, together with similar dimensions of window holder, and viewing port in a graphite block. It was found necessary to enclose the arc standard with a metal box with no roof, to prevent draughts from disturbing the arc.

4-C Experimental Procedure

The experimental techniques used during a run were gradually evolved from rather crude operations during the early runs where only a few of the relevant observations were made. The procedure developed, which was used in all runs where quantitative results will be quoted, was not established until the 50th run. By this time, all calibrations had also been made. The fully established technique is reported below.

C1 Preparation

The solutions in the gas bubbling train for acetylene analysis were replaced if this was needed, and the system checked with a known sample of acetylene. Anode rods were gently sanded so that they all fitted through a test hole the same size as that in the reactor, and their ends machined so that they fitted into each other. The reactor assembly was put together, ensuring that the anode tip was in the same horizontal plane as the cathodes, with cathodes each 3 mm from the anode, and reactor, quench and cooler were tested for gas leaks. The various parts of the reactor were also tested for electrical insulation. The hydrogen flow was turned on at 18 g hr^{-1} for half an hour to flush out the system, and the burner lit. One hydrogen flow was fed to each cathode, as will be discussed in chapter 5, and these flows were balanced. The potential difference between the quench tube and earth was measured using a high impedance voltmeter, with the full supply voltage across the arc gap. Water was turned on at the calibrated settings, and care was taken that the

thermocouple readings had reached steady-state before starting the run.

The spectrograph plateholder was loaded and placed on the spectrograph. Finally, the hydrogen flow was adjusted to the desired level, and switches were closed on the resistor bank according to the current required.

C2 Run

All readings of instruments and other observations were recorded as the run progressed, on to a tape. The taperecorder was actuated from the hand microphone. Even when this method was used, important measurements were sometimes still lost, owing to lack of time during the run.

With the supply voltage between anode and cathodes, one cathode was brought in to touch the anode, and drawn away quickly to its operating position 3 mm from the anode perimeter. The arc thus formed was restricted in current to 10 to 20 A for 5 minutes at ~~the~~ start of each run, in order to have the arc chamber hot before measurements were made. An image of the anode and arc was projected on to a screen set around the spectrograph slit, by the spectrograph lens. This image enabled the operator to vary the anode feed so that the front face of the anode remained at the same position in the field of view, no matter what the current. The normal position of the anode tip corresponded to an actual position 10 mm below the cathodes.

After 5 minutes, the current was changed to that desired for the run. Arc voltage, current, power, mass flow readings were taken from this time at least once every $\frac{1}{2}$ minute.

After the reactor cooling water temperature increase had settled to a steady value, as indicated on the strip chart recorder, the sample valve was pushed to take a sample for acetylene analysis, and a sample was taken by syringe for the gas chromatograph. Care was taken that the air to the ejector pump was adjusted correctly so that the product flow at the sample valve was at atmospheric pressure, as seen by a manometer. After 5 minutes, the bubbler train selector was moved to direct the carrier gas flow to another set of bubblers, and the sampling valve barrel withdrawn to allow the product gas to flow through its sampling loop. After another minute, the sampling valve was pushed in to take another sample. Samples were taken in this fashion until all four bubbler trains were used, or the run ended.

Checks were made during the run, of water flows, of quench tube voltage and of reactor pressure. Depending on the purpose of the run, several spectrograph exposures were made, using a rotating sector driven by a synchronous motor to give an accurate exposure time. Other measurements occasionally made were that of total radiation intensity from various positions in the arc using a thermopile, and temperature of the graphite walls, using a chromel-alumel thermocouple.

It will be shown in the next chapter that a large proportion of runs ended in difficulties before more than two samples were taken and only towards the end of the work were conditions sufficiently controlled that the run was ended only to analyse the samples.

To end the run, the current was switched off, hydrogen flow stopped after 5 minutes, and water flows shut down after 15 minutes, when it was observed that the reactor had cooled.

C3 Analysis of Run

Within minutes of shut-down, the silver nitrate solutions were titrated with alkali for estimations of acetylene. The soot filter was undone, and the soot weighed if the amount was at all appreciable. The reactor was taken apart, in latter runs only down to the end plate flange, and any carbon on the floor of the chamber, or in the quench tube was collected by a small "vacuum cleaner" arrangement, and weighed. Damage, if any, was assessed, and all components of the reactor were tested for appreciable electrical paths between them by an Avometer. Samples of product gas were analysed with the gas chromatograph, and all observations made during the run were transcribed word for word onto paper.

References Chapter 4

1. "Standard Method of Test for Alpha Acetylenes in Butadiene, Butadiene Concentrates, and Butane-Butene Mixtures, Silver Nitrate Method" Stand. Am. Soc. Test and Mat. ASTM D1020-61 (1961).

2. Sutton, G.F. Project Report for Final Year of B.E. (Chem.) 1969.

3. Hattenburg, A.T. "Spectral Radiance of a Low Current Graphite Arc" Applied Optics 6 No.1 (January 1967) 95-99.

RESULTS - REACTOR MODIFICATIONS AND WORKING EXPERIENCE

CHAPTER 5

The modifications made to the reactor geometry to achieve a workable design are listed below. There proved to be three main problems to be solved.

(a) survival of the anode insulation

(b) electrical insulation around the reactor walls

(c) cathode operation with no carbon build-up

The important features of the experimental runs will be given where pertinent to the success of the design. The initial choice of materials for reactor components proved to be satisfactory.

Run No. Comments

1-8 Fig.5.1 A black conducting layer was found on the top of the boron nitride insulator, fusing it to the anode. The insulator quickly eroded through, apparently as the result of the arc being transferred to it. The theory that such reaction of the boron nitride was with pieces of carbon fallen from the anode, which fed vertically upwards, was tested by inverting the reactor, so that the small pieces observed coming off the anode would drop out of the reactor. The small pieces were removed, but damage to the insulator was similar, so the reactor was henceforth run with the anode driving vertically upwards. It was thought that the buoyancy of the arc would help with this orientation, and the problems of holding the anodes in place would be smaller. When the arc was left to wander from the anode for more than a few seconds, the arc chamber became filled with a frothed clinker. When the anode rod was

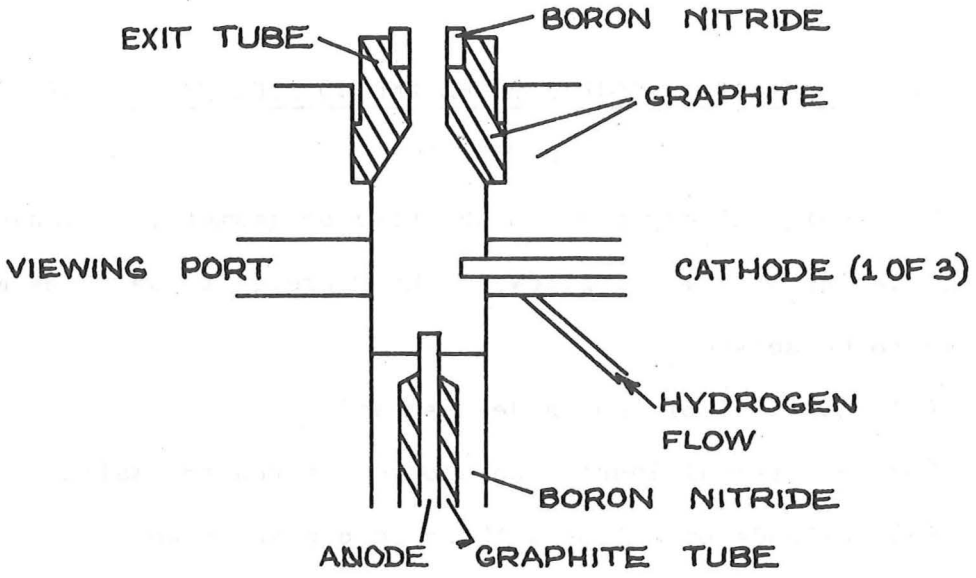


FIGURE 5.1 INITIAL CHAMBER CONFIGURATION

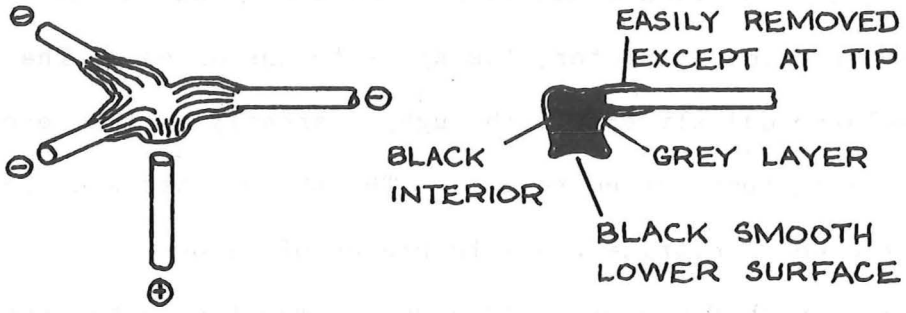


FIGURE 5.2 DEPOSIT ON CATHODES

inadvertently advanced beyond the plane of the cathodes while the arc arc was out, and the arc restruck, the anode was eaten through where the arc was struck, and a piece of the rod fell to the chamber floor. This commonly caused a short circuit. However if the anode was advanced to the same extent while the arc was operating, the arc remained attached to the front face of the anode. A hydrogen flow corresponding to an atomic ratio of C/H of 1 was first used, but because of carbon deposit troubles, the hydrogen flow was increased so that C/H $\simeq$ 1/4 to 1/12 atomic ratio, or 3 to 1 mass ratio, was used. The exit to the arc chamber was made as a separate piece of graphite which was inserted into the main graphite body, for convenience of assembly. This had the effect of thermally insulating the tube, so that it operated at a much higher temperature than the rest of the chamber. Over a number of runs, the outside surface of this tube receded several mm and had a crystalline appearance, with crystals of the order of 1 mm in size.
The arc chamber layout at this stage is shown in figure 5.1.

After some practice, the arc could be operated for about 15 minutes with currents from 20 - 40 A, but large formations of a dense material occurred on the cathodes, eventually closing the anode-cathode gap so that the arc was extinguished. The growths were bulbous in form (figure 5.2), had a light grey surface with small ridges running in the direction of growth, and a black, smooth interior. The bottom of the growth, presumably where the arc had attached, was also smooth and concave downwards toward the arc. Even when the growth was

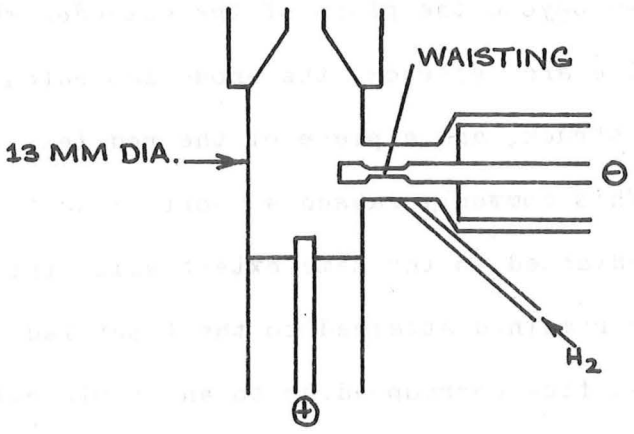


FIGURE 5.3

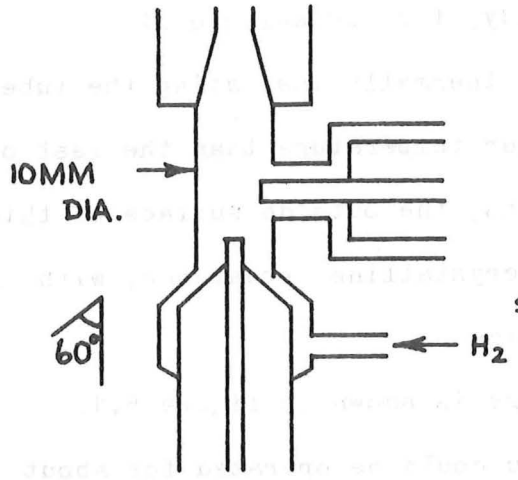


FIGURE 5.4

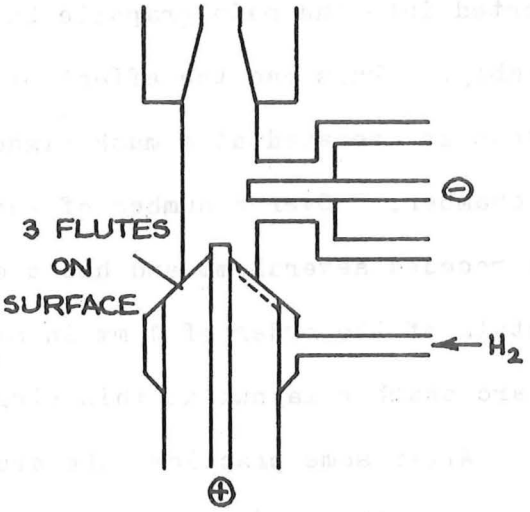


FIGURE 5.5

electrically in contact with the anode after a run, it could be lifted off with ease, and was still smooth on the underside.

9-10 Fig.5.3 An attempt was made to vaporize the carbon (or whatever material it was) off the cathodes as it formed. The conduction path for heat transfer back from the tip was narrowed, by grinding a waist in the tungsten of 1.5 mm diameter for 6 mm, starting 6 mm back from the tip. No deposit formed on the cathodes, but for currents around 40 A, the tips melted and deformed excessively. With most runs, deterioration of the BN cap around the anode occurred, as could be observed during the run by a change from the blue colour which was normal, to a pink streak from the position of the BN. The cathode problem was ignored for the time being, and the anode configuration changed.

11-12 Fig.5.4 In order to keep the BN cover clear from any carbon vapour which may have diffused to it, the hydrogen flow was introduced past it. Also the diameter of the chamber was reduced, to obtain a faster and more streamlined flow. Burn-out was just as severe.

13-14 Fig.5.5 Both a faster hydrogen flush, and more effective cooling for the BN, were intended by having the BN cap hard against the graphite block, which did not even run red hot. The hydrogen flowed in through three flutes in the surface of the BN cap. Partial success was found at 40 A, for the area of BN around the flutes was clean, but 1 or 2 mm of carbon

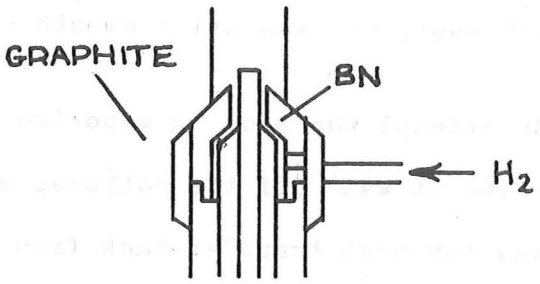


FIGURE 5.6

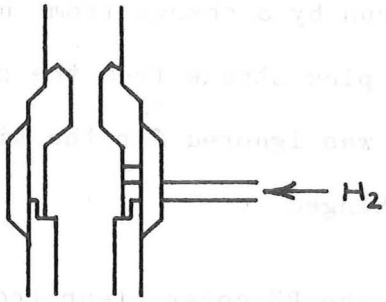


FIGURE 5.7

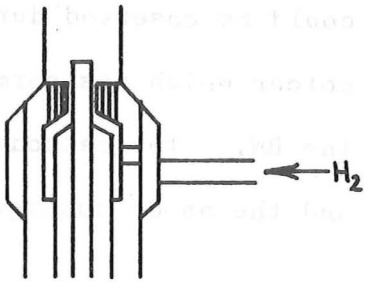


FIGURE 5.8

deposit formed on the BN close to the anode. A well controlled run at 60 A was made, but after a couple of minutes severe deterioration of the BN was observed again.

15 Fig.5.6 Having established that a hydrogen flow was beneficial, the flow was then introduced around the anode itself. Arc operation became less stable especially at low currents. After a 55 A run, some damage and carbon reaction was seen on the BN around the anode hole.

16 Fig.7 The two aspects, adequate surface irrigation with hydrogen, and adequate cooling, were emphasized in this design. A small crater was formed on one side of the BN cap after the arc was observed to jump from the anode a couple of times just before the end of the run. It was concluded that a conducting layer was still forming on the BN cap, and the arc was transferring to this to bypass the hydrogen stream. Provision was made to project an image of the flow through the exit tube on to the viewing screen. A reddish glow of the gas flow, together with bright orange streaks signifying large hot carbon particles, was seen. With some of these runs, little deposition was found on the cathodes, which were bright and melted at the tips. Some spattered metal was found at times on the chamber walls near the cathodes.

17-19 Fig.5.8 To provide better distribution of hydrogen over the surface of the BN, many small holes were drilled through the cap surrounding the anode. After short runs at 35 and 55 A,

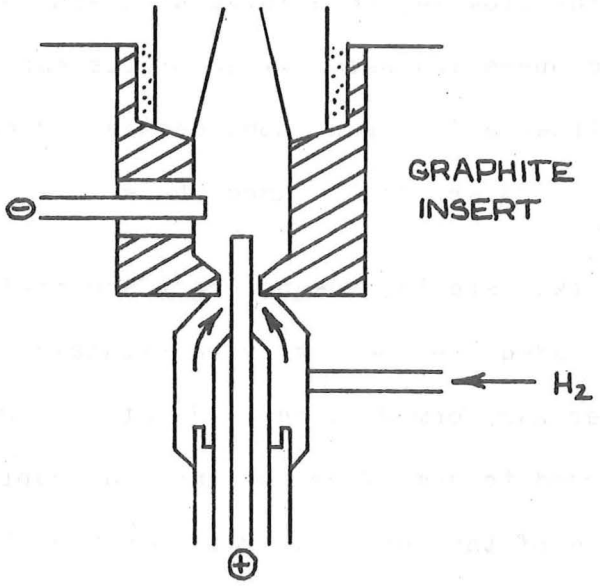


FIGURE 5.9

the BN surface was clean, except for some light coating around the central portion. After several minutes of running, the BN cap was cleanly eaten away close to the anode. This perhaps was caused by the radiation from the arc and anode, together with poor cooling, which sufficed to bring the BN to its decomposition temperature. During these runs, the cathodes appeared to remain clear of deposit until they had deformed by melting into a larger mushroomed tip. Rapid deposition was then observed, so that the cathode-anode gaps became quickly bridged with the material previously described. It may be significant that when the graphite exit tube was further thermally insulated from the main body by a gap and MgO powder, some deposit similar to that observed on the cathodes appeared on its surface in isolated lumps. Normally a slower build-up of material occurred evenly over its inside surface, or not at all, depending on the carbon feed rate. This deposit formed a smooth surface which looked like a carbon, (black, could be machined) but was much more difficult to file away than the exit tube graphite, and was stronger.

21-23 Fig.5.9 It was proposed that the BN cap was not necessary for insulation around the anode, and that the hydrogen flow, at a sufficient velocity, was sufficient to keep the arc from wandering to the walls. To test this theory, graphite was substituted for the BN cap. With a low current (11 A) the arc operated on the anode very steadily for 5 minutes, and then suddenly jumped out of view. It was found that the arc had divided into two. The current was carried from the cathode

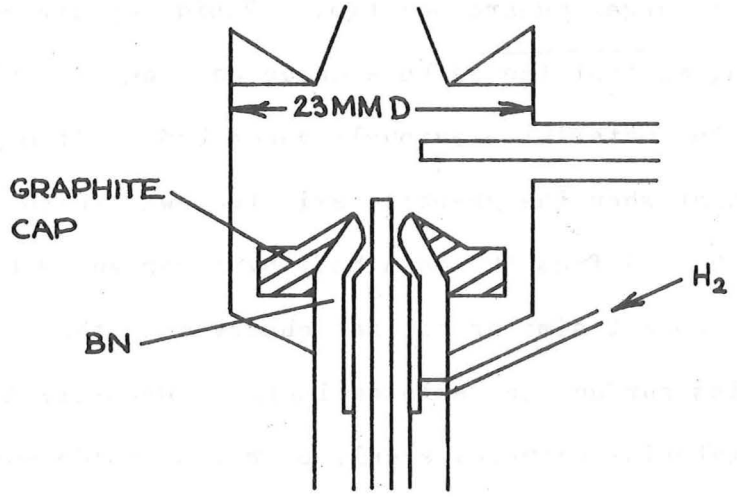
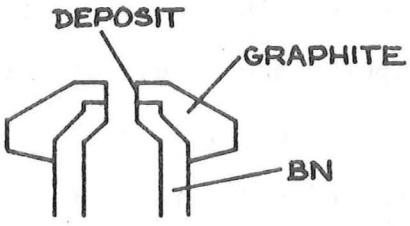


FIGURE 5.10

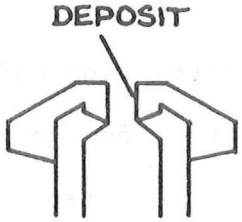
to the graphite block by arcing, and similarly from the graphite block to the anode. However, there was a possibility that the cathodes touched the graphite body accidentally during the run. The gaps from cathodes to the walls, and from the anode to the wall, were widened to about 1.5 mm. A similar result obtained, except that the arc bypassed the cathodes entirely, and attached itself to the quench tube from the graphite exit tube, making the quench tube an auxiliary cathode. It did this on the plasma stream side of the BN insulating collar. A large number of holes of the same size as those used with the BN cap were then drilled in the graphite web around the anode so that the hydrogen flow passed axially through them as well as through the gap surrounding the anode. In this case, also, an arc occurred easily between the anode and the graphite wall. It was concluded that an insulating surface was necessary around the anode.

24 Fig.5.10 From the above experience, it was decided that the graphite walls would be moved away from the arc to provide a less attractive alternate path for the current, to provide another insulating gap, (making three between anode and cathode) and to reinstall the BN cap with a protective graphite cap on it. Since the conducting layer on the BN seemed unavoidable, it was best to put it to some use, and prevent radiation damage on the BN surface. The arc ran well, until extensive deposit formed on all cathodes, bridging the arc gap. The graphite anode cover was loaded to a small extent by hard carbon deposit on its top side, whereas the BN cap was undamaged, except for a



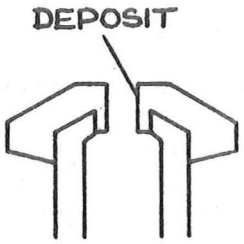
NO ARC-BACK

(1)



NO ARC-BACK

(2)



ARC-BACK

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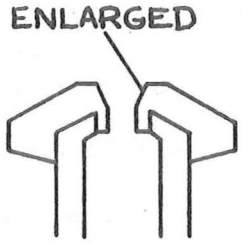


ARC-BACK

(4)

FIGURE 5.11

small area around its forward lip where it was exposed to the arc. Ideas that the cathode deposits derived in part from the BN present, were disproved by the results of this run, as almost no BN was vaporized.

25-27 Fig.5.11 The BN cap was completely protected from arc radiation by extending the graphite cover. This resulted in no damage at all to the BN, but a carbon deposit formed around the hole in the graphite cover, so that the hole became too small for the anode rod. An interesting observation was that the exit tube was not above a dull red hotness for a current of 10 A, but was at an orange heat for a current of 30 A. Various small modifications to the graphite cover were made, bringing the graphite down into the BN cap so that the wall of the cap was lined with graphite, and widening the hole through which the anode passed. The latter was done to prevent build-up closing the hole too rapidly. Arc-through to the anode supporting tube occurred. The rapid flow of cold hydrogen through the hole may have prevented arc-back while the hole was small, but once the hole had been widened, this deterrent was not so strong, perhaps allowing arc-back to happen. However, the arc attached itself to the anode tube when first the BN was removed from the underside of the anode cap, exposing graphite, before the anode was widened. Thus the presence of the graphite layer which could 'see' both the arc and the anode tube was a major cause of arc-back, at least, in support of experience with the graphite walls.

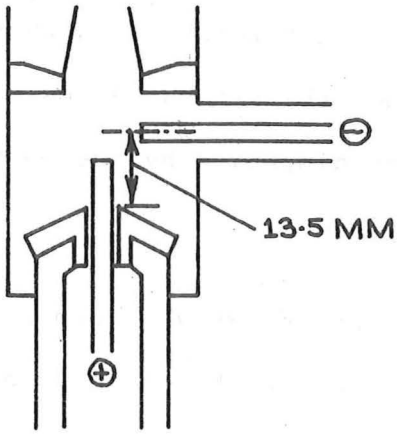


FIGURE 5.12

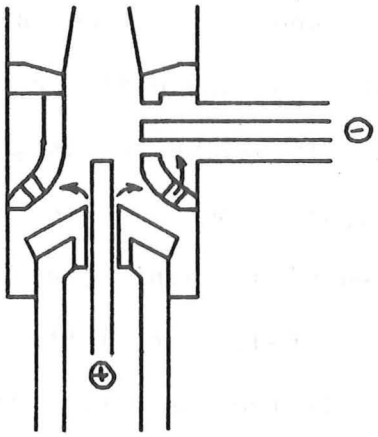


FIGURE 5.13

28 Fig.5.12 An attempt was made to reduce the risk of arc damage to the anode by bringing the anode assembly, back from the anode tip. A long run was achieved, without arc-back. It was noticed that the arc extinguished when the gap between anode and cathodes became more than about 10 mm for the lower currents (15 A), but was stable for higher currents. The BN cap was unmarked, but a metallic looking surface was observed on the underside of the graphite cap, apparently from reaction with the BN in contact with it.

29 Fig.5.13 A graphite insert was used. This acted as a radiation shield, and it was hoped, would direct the flow of gaseous carbon in towards the centre, avoiding much contact with the cathodes. The apron of the insert was widened towards the anode, with the aim of preventing the arc from jumping to it. A long run (15 min.) was achieved at a low current, with little deposit on the cathodes. The results were complicated by a failure of an anode to anode spigot-in-hole electrical contact, causing an arc to develop beneath the anode cap. The anode arrangement was then changed so that an all-BN face was presented again on the cap underside, as in figure 5.11. After running at a high current for a short while, deposit had built up on the cathodes, and bridged the arc gap. Thus the radiation and flow baffles did not help the cathode problem.

31-32 With the same configuration as before, graphite rods of the same diameter as the tungsten cathodes replaced the latter,

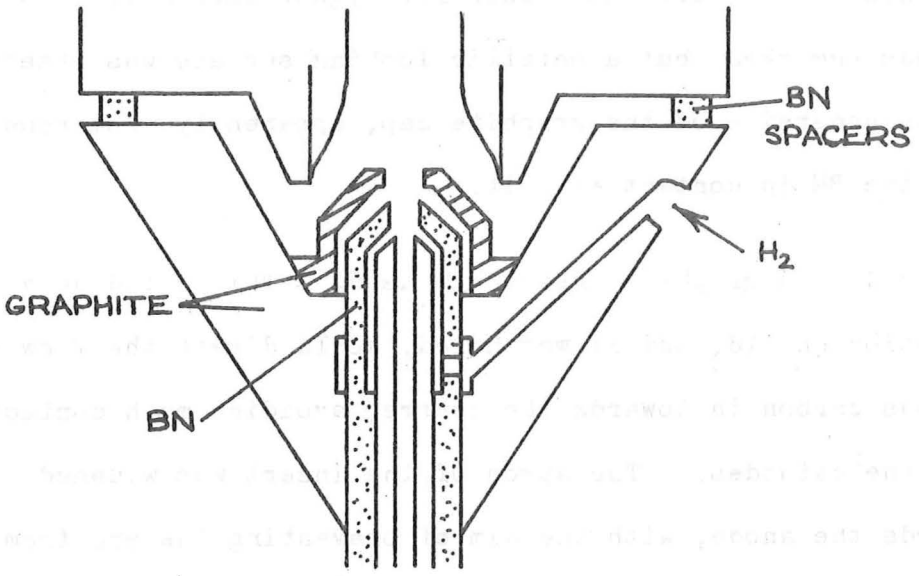


FIGURE 5.14

thus testing whether the tungsten was peculiar in allowing or causing a deposit. Deposits of the same size and appearance occurred on these graphite cathodes for the same carbon feed rates as those used with tungsten cathodes. It was significant that for currents of only 10 A, the graphite cathodes were removed at the rate of about 1 mm minute^{-1}, whereas for a current of 30 A, where carbon loss from the anode was rapid, the cathodes rapidly built up. Problems were found where flakes of carbon accumulated around the BN cap, and caused the current to pass through the graphite insert and body.

33-37 Fig.5.14 The requirements of the anode surround were

(a) an insulator such as BN covering the anode electrical contacts,

(b) a cover on the BN to prevent both radiation damage and the deposit of a carbon layer on it,

(c) no chemical reaction of the cover with the BN,

(d) a sufficient flow of cold hydrogen to prevent the arc from running back down the anode to its electrical contacts,

(e) a third insulating gap removed from the arc space, and so unlikely to arc across.

These requirements appeared to be met by the design in figure 5.14. No undesirable arcing occurred with this configuration, except when sufficient carbon deposited on the graphite cover around the anode hole to close it on the anode, and carry the cover up with the anode. This trouble was eliminated by enlarging the hole and providing a gap of about 1.5 mm around the anode. The boron nitride insulator

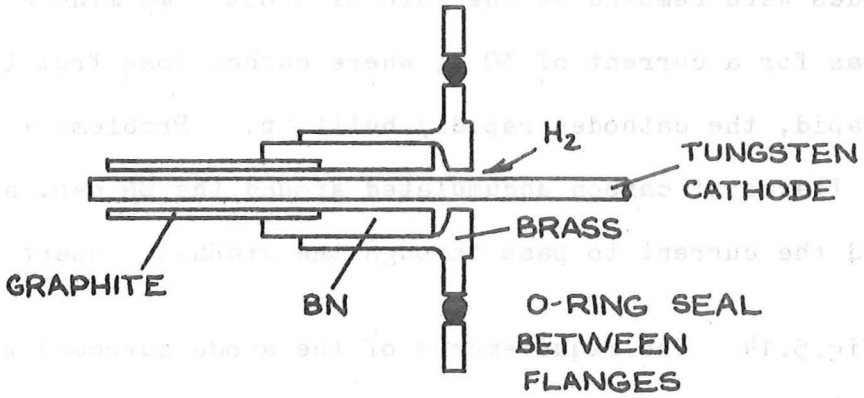


FIGURE 5.15 CATHODE ASSEMBLY

remained clean, and in fact this arrangement was undamaged for the rest of the experiments carried out on the reactor.

Problems were still unsolved with the cathodes. Difficulty was found in controlling the position of the tips of the graphite cathodes, as they either eroded or built up. The arc became unstable, and frequently extinguished, presumably from the dissymmetry of the cathode tips.

Indications were seen that hydrogen flow around the cathodes prevented build-up of material after holes were made at the bottom of the radiation baffle so that hydrogen could circulate up past the cathodes. After a run, deposit was observed on the back side of the radiation shield, but only well away from the likely route of hydrogen. Also the cathodes were almost clear of deposit.

38-41 Fig.5.15 The clue provided above was followed up by making an extensive change to the cathode assemblies to allow hydrogen to be fed to them independently from that flow to the anode. Graphite tubes carried the hydrogen in annuli around the cathodes, forward to within 2 mm of the cathode points. Initially the hydrogen flow was uncontrolled between cathodes. It was decided to revert to tungsten as material for the cathodes.

After a run, two cathodes were found clean, with slightly melted tips, and the other built up with deposit. It was also found that the flow of hydrogen through the third cathode assembly was much less than that through the other two.

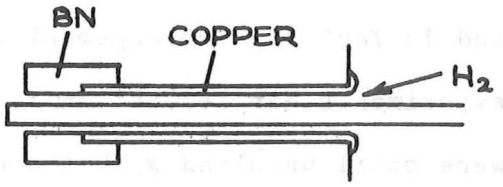


FIGURE 5.16

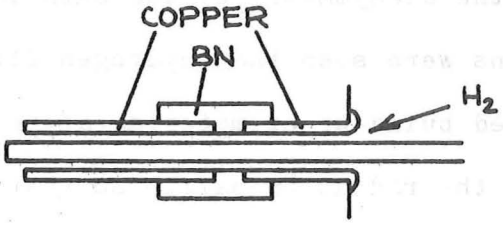


FIGURE 5.17

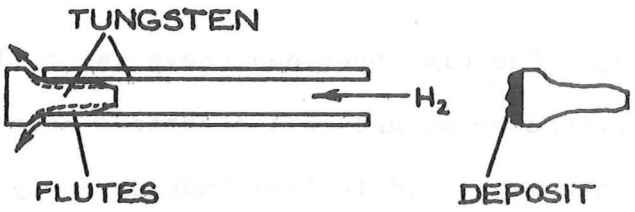


FIGURE 5.18

Thus the conclusion may be made that the hydrogen flow was required to be some appreciable size to avoid deposition. However, if the carbon deposition depended on the current to the cathode, and it appeared that it might, for no similar deposition occurred on the walls, then this would rather or also indicate that the current was unevenly distributed, and so cause uneven deposit. To decide between these alternatives, (rather or also) it is suggested that the hydrogen stream tends to blow the arc away from a cathode, and so the distribution of hydrogen to the cathodes determined the distribution of current. Through this effect, and perhaps by reaction also, the hydrogen flow may have controlled the deposition the way it did.

Trouble was experienced with arcing across the graphite sleeves, which were also not sufficiently robust to allow much handling.

42-44 Fig.5.16 Insulation of the hydrogen-carrying tube from the cathode was attempted, so that the arc was prevented from jumping back to the tube. The BN insulator could not be taken closer to the cathode tip than about 4 mm for fear of damage from arc radiation. Deposit formed in large quantities on the cathodes, and the conclusion was made that not sufficient hydrogen was reaching the tip surface.

45 Fig.5.17 A graphite tube was inserted into the BN insulating bush, to carry the cathode hydrogen flow forward to the cathode tip, but even with the electrical insulation of the graphite

tube from the cathode, the graphite tube was destroyed quickly by arcing.

46-62 Fig.18 The hydrogen carrying tube was made the electrical conductor, and made from tungsten so that it was robust. A tungsten tip was inserted into the end of the tube, with flutes ground into its shank so that hydrogen could be flushed past at two points on its perimeter. The tube was made from a 6.6 mm (1/4 inch) diameter tungsten rod, which was drilled with a drill of 4.2 mm (5/32 inch) diameter. A much improved performance of the cathodes was obtained. Runs as long as 25 minutes at 30 A were obtained with negligible deposit on the cathode tips except towards the end of the run, when sudden rapid build-up joined the cathodes to the anode. At other times, only short runs were made before the same happened, signifying that there was a factor in the problem which was not controlled. Deposit occurred only on the front face of each cathode tip, while its shank showed a clean, coloured surface. The colour of the tungsten shanks varied from its colour when at room temperature, through brown, violet to blue. The blue colour appeared when the tip had melted, indicating that the colour was a measure of the temperature it reached while operating. It was noted that where one cathode was preferentially built-up with deposit, it commonly had a shank of a light metallic colour, which was interpreted as meaning that it had been cooler than the others. The tungsten tube was almost clean in all runs.

Arcing from the graphite exit tube to the quench tube caused more trouble, and it was realised that the exit tube, being in the path of the plasma flow, was acting as an auxiliary cathode. It was thus insulated from the cathode from run 54 on. However positive voltages appeared on the quench tube of about 40V, due to leakage resistances when the arc was out, but also due to the influence of the arc when it was on, for the voltage rose to 48V during a run. A 50 KΩ resistor was placed between the quench tube and cathodes which kept the quench tube voltage at about +20V maximum. It was noticed that the arc extinguished itself frequently without the leakage resistor in place.

After several lengthy runs some smooth deposit of carbon was observed on the exit tube as shown in figure 5.19.

64-75 Fig.5.20 The solid tungsten cathode tip was replaced by two halves, with a flute ground on the inside of each half running the length of it, to allow hydrogen to flush across the face of the tip. It was thought that porous tungsten would have been ideal for this application, but it proved difficult to obtain. At times, the arc extinguished easily at 20 A, but was sufficiently stable at 30 A. Gradually deposit formed on the lower lip of the front face of the cathode tip, so this lip was reduced in size by grinding, to allow hydrogen to irrigate the surface more effectively. Less deposit was formed.

It was noted that the power of the arc decreased just

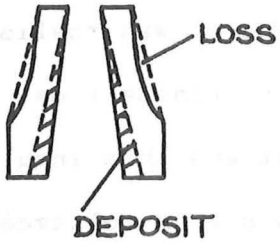
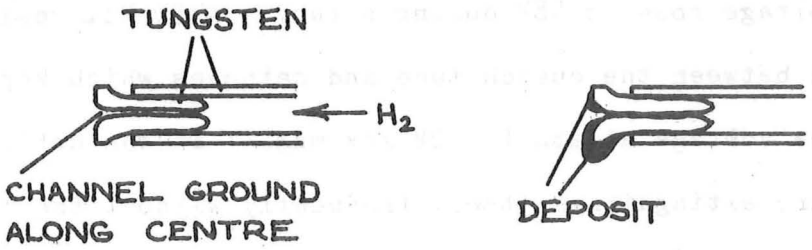


FIGURE 5.19 GRAPHITE EXIT TUBE



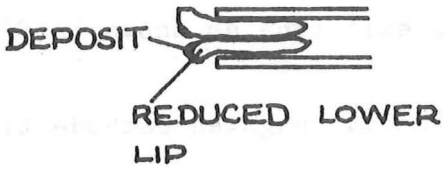


FIGURE 5.20 SPLIT CATHODE TIPS

before a deposit appeared on the cathodes. It was first suspected that the drop in arc voltage accompanying this (86 → 65V), was caused by the shortening of the arc due to the deposit on the cathode. A run was stopped as soon as this drop in voltage became steady. Deposit had formed on the cathodes completely covering the central passage, but was much too small an amount (1 mm) to significantly shorten the arc. The highest voltage gradient one can assume here is that for the hydrogen arc ($4V\ mm^{-1}$) (1). A mere shortening of the arc by 1 mm could thus reduce the arc voltage by only 4 to 5V. The drop in voltage was thus thought to be related to either the change in electron emitting surface, or the blocking of hydrogen flow to the front face. It was seen from the run before, where a single solid tip had been used on each electrode, that the voltage had dropped to the same extent for an end-of-run deposit of about the same size. The second alternative was therefore eliminated.

The electron emitting properties of a surface depend on its work function. The author was satisfied that the deposit on the cathodes was some form of carbon, as no BN decomposition occurred, and little tungsten was lost from the cathodes. Little difference was thus expected in emission from the cathode in changing from a tungsten surface to the carbon deposit surface, since the work functions are closely similar (W 4.5V, polycrystalline graphite 4.6V). Electron emission increases rapidly with temperature. The sublimation point of carbon is about 4100K, compared to a melting point of 3680K for tungsten.

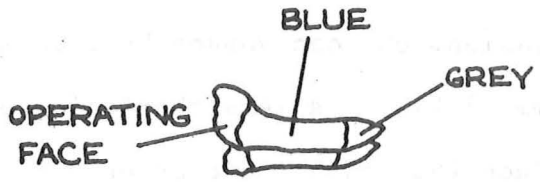


FIGURE 5.21 A SPLIT CATHODE

TIP AFTER 'CLEAN' OPERATION

It is expected that the tungsten surface, however, would operate above the melting point, perhaps even to the boiling point at 7000K. This matter of a drop in arc voltage to the extent of 20V when deposition began to occur, will be taken up in chapter 7. It is sufficient to say here that it must be a gas phase phenomena, and not some behaviour within the cathode or anode themselves (e.g. contact potentials), because of the size of the voltage change.

Some significant observations were made on the cathode tips. After one run, one cathode tip was much cleaner than the other two. The clean tip had a blue shank as in figure 5.21, whereas both tips with deposits had grey shanks. As this appeared to indicate different rates of cooling, probably dependent on the hydrogen flow through each tip, the size of each flow was determined. It was surprising to find that the two deposited cathodes had flow rates of 4.4 and 0.4 g hr^{-1}, whereas the clean cathode had an intermediate flow of 3.4 g hr^{-1} (45A run). To test roughly the significance of the surface colour on tungsten with relation to temperature, a tungsten rod was heated mildly with an oxy-acetylene torch (in air), during which the blue-green colour appeared on the grey surface. On further heating with the same torch, the blue coloration disappeared, and a yellow colour appeared before a cherry red heat was reached. The blue colour was interpreted to be tungsten hemipentoxide in both the flame and the reactor (2). The hemipentoxide begins to sublime at about 1100K, indicating a low cathode operating temperature.

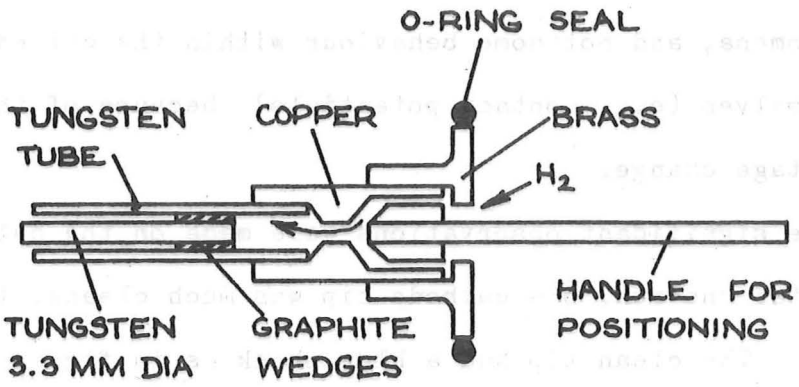


FIGURE 5.22 FINAL CATHODE ASSEMBLY

69-75 Measured hydrogen flows were used at the cathodes, and each flow was balanced with the others before a run started. Three small rotameters were calibrated for the 0.5-5 g h^{-1} range. Several runs were done with the cathode flows set at values between 2 and 3 g h^{-1}. These runs were characterised by widely fluctuating arc voltages from 90 to 150V, and frequent extinguishing of the arc. The current fluctuated with the voltage, causing the rate of carbon ablation from the anode also to change. The runs with cathode hydrogen flows of 2.0 g h^{-1} for a total current of about 20 A resulted in bright clean cathode tips with some slight melting and blue coloration. While these runs looked promising, the difficulty of maintaining the arc prompted a further change in cathode design. It was suspected that the bad electrical contact found at times with a resistance meter between the tips and the tube may have contributed to the arc extinguishing.

76-84 Fig.5.22 Better electrical contact was aimed for in a design which was similar to that used before in run 45, and used at this stage with better control over hydrogen flows. Features of these cathodes were the graphite wedges holding the tungsten rod firmly central in the tungsten tube, and thermally insulating the rod to some extent, so that the rod ran hotter. Initially the same trouble was had with the arc extinguishing many times, and the arc voltage reaching 150V with an average of about 120V. Cathode hydrogen flows were from 1.6 to 2 g h^{-1}. However, stable operation was obtained by keeping the anode tip well forward for the lower current runs. For a 20 A run, the

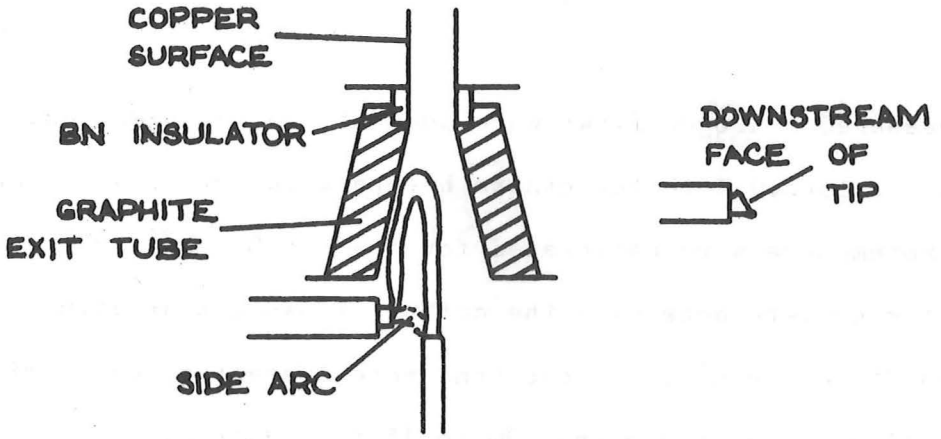


FIGURE 5.23 SUGGESTED ARC BEHAVIOUR

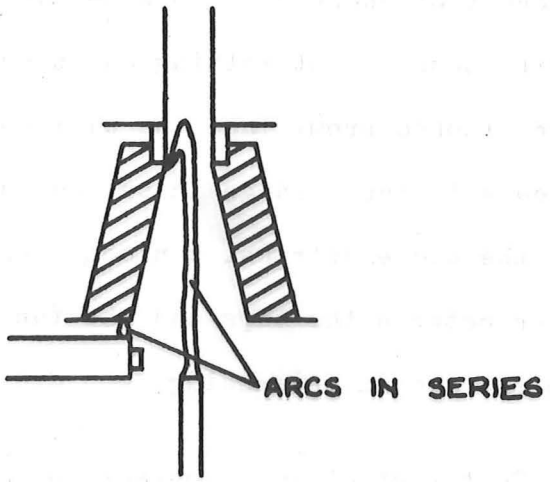


FIGURE 5.24 A POSSIBLE EXTINGUISHING MECHANISM

anode tip was no more than 3 mm upstream of the cathodes for stability (100V steady), whereas for a 40 A run the anode could be brought back to the customary 10 mm below the cathodes for stable operation at 95V. After runs of 20 minutes, only a dark coloration, assumed due to carbon, appeared on the tips of the cathodes. After one run where some deposit was found, the cathode rod was blue in colour towards its rear end, but grey towards its forward tip.

For all runs from run 80 onwards, care was taken in the placing of the cathodes. The standard position of the tips became three points on a 10 mm diameter pitch circle. It was noticed that if the anode was allowed to move past the cathode plane, the arc voltage rose by about 20V. This focussed attention on the voltage measurements of the quench tube, which was approximately +8V relative to the cathodes for normal arc voltages (95V). The quench tube voltages followed the arc voltages, being consistently 8% of the electrode-electrode voltage even when the arc was not running, and since this could be explained by leakage resistances in the reactor structure, it appeared that the arc did not directly affect the quench tube voltage with a 50 KΩ leak resistor attached. This contrasts with the observations made in run 80 without the leakage resistor attached. Thus any current to the quench tube from the arc or plasma flow would be less than 1V/50 KΩ = 20μA. It is probable that the arc itself did not reach into the quench tube, which would then have acted as another cathode.

It is proposed that the arc was carried upwards by

convection at the lower currents, to form a loop constricted on one side by the graphite exit tube, as in figure 5.23. At these lower currents, the arc was observed to reach vertically from the anode out of sight of the viewer, and to attach on the upper side of the cathode. Some evidence for this looping was also given by the melted patch on the cathode tip facing downstream after low current runs. The rapid drop in arc voltage down to 50V observed occasionally could be explained by a direct arcing (dotted in figure 5.23) between cathodes and anode, similar to the behaviour observed with plasmatrons.

Some light arcing paths were observed on the outside of the cathode tubes, running about 10 mm along the length of the cathode tube back from its tip, and corresponding arcing paths were observed on the inside of the holes in the graphite radiation shield and body, in which the cathodes lay. Since these marks were only light, they could not have been associated with steady operation of the arc. There were only one or two of the tracks observed after a run, so that it is likely that they were associated with the extinguishing of the arc. A possible mechanism is illustrated in figure 5.24, where it is suggested that the arc attached from the cathode tube to the underside of the graphite exit tube support, and sufficient electrons were emitted from the hot exit tube (a temperature of 3300K is needed) for the arc to attach itself to the upper end of the exit tube. Since this was a surface over which gas flowed with high velocity, the arc would have become liable to be blown away from the surface, and to be extinguished.

85-86 The total gas flow rate was reduced from 18 g h^{-1} to 10 g h^{-1}, in an effort to reduce the possibility of arc blow-out caused by the above mechanism. Unfortunately the arc extinguished as frequently as before. It was noticed that the quench tube voltage rose suddenly from the 6-8V which was normal, to greater than 50V, (full scale reading on the voltmeter was 50V) just before the arc went out, and then returned to normal when the arc had gone. This behaviour was observed two times, and towards the end of the run, the quench tube voltage was seen to be greater than 50V while the arc was not operating, but returned to normal when the arc was started again. If one associates the increase in quench tube voltage with a mechanism of extinguishing the arc, then it appears that the mechanism was not the one worked out above, for a large increase in quench tube voltage according to the above requires the arc to be operating. After the run it was found that a bridge of "pyrolytic" carbon 3x2 mm had formed between the web of the radiation shield and the anode, making the graphite arc chamber positive at the same potential as the anode. Also some metallic material (presumably tungsten) was layered around the bottom of the exit tube on its inside surface just above each electrode, and was more pronounced above one than the others. The build-up causing the positive potential of the quench tube (identified with solid-solid contact with the anode) at the end of the run, was not present during the previous positive potential observations, for the anode was free to move.
A possible mechanism for arc-out, suggested by the small pieces

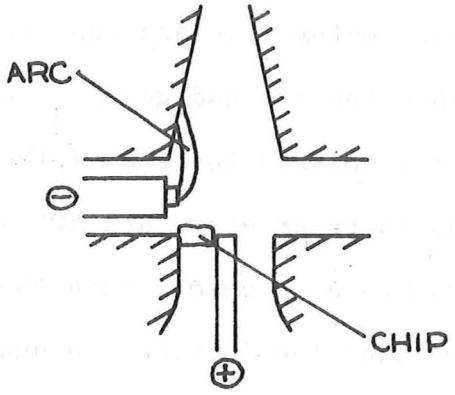


FIGURE 5.25 A POSSIBLE EXTINGUISHING MECHANISM

of leaf carbon found on the chamber floor, is shown in figure 5.25. The anode was off-centre in the graphite body by 1 mm, leaving only 2 mm to be bridged by leaf carbon, which was commonly 4x2 mm. The leaf carbon was observed during operation of the arc at 20 to 30 A, peeling sideways off the anode from around the anode crater. It is suggested that the leaf carbon touched the chamber wall occasionally as it peeled off, making electrical contact. To follow the stream, the arc would tend to attach upstream of the cathode, thus attaching to the bottom of the exit tube. Depending on the comparative rates of deposition and loss of carbon from the leaf bridge, it could then 'burn' out, or build into a more secure contact. Burning out would interrupt the arc, but this would be likely to start again from the single arc where the bridge had been. If the leaf carbon made only momentary contact, and then was blown away, the two small arcs created on either side of it would very effectively quench the current. The solid bridge found at the end of the run may have been started by such a mechanism.

To avoid the possibility of arc-out due to leaf carbon, the web of the chamber wall below the cathodes was removed so that an extra 1.5 mm space existed between the anode and the nearest part of the wall, giving it an inside diameter of 13 mm. Also, to prevent the possibility of collection of carbon on the graphite anode cover, the latter was reduced in height off the chamber floor, from 10 mm to 8.5 mm. With these alterations, but the same conditions otherwise, the arc was still blown out frequently. It was noticed that the arc voltage climbed much

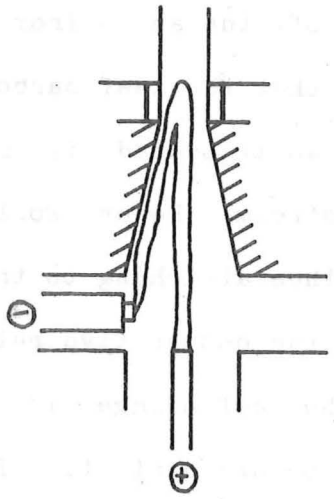


FIGURE 5.26 AN ARC BLOW-OUT MECHANISM

higher than in the previous run, to 150-170V compared to an occasional maximum of 130-140 in the previous run. The voltage was observed to vary in slow cycles of period about 5s, from around 100V up to 150V and then down to 100V again. Occasionally the voltage remained at the upper voltage for 30s, and at all times when the voltage was being observed during an arc-out, it was noticed that the voltage had reached a value equal to or above 150V. This contrasts with the previous run, where voltages of 80V were observed on the voltmeter as the arc current stopped.

The above observations suggest that the carbon leaf mechanism of extinguishing the arc had been eliminated, and that a mechanism remained which consisted of lengthening the arc until it was blown out. This would be similar to that proposed before and described in figure 5.24, except that an attachment to the exit tube could not be invoked, for no arcing marks were found on the bottom end of the exit tube. It is proposed that the arc simply extended upwards due to forced and natural convection, probably laying close to the inside wall of the exit tube, and became unstable at a sufficiently high voltage compared to the supply voltage (figure 5.26). More often than not, the arc voltage returned to a lower value, indicating that a more favourable path for the arc had been found. With three cathodes, and some turbulent and varying flows within the arc chamber, it would appear easy to find alternative paths within the chamber. It will be argued later that the ionization potential is lower in the presence of carbon than in pure hydrogen, so that

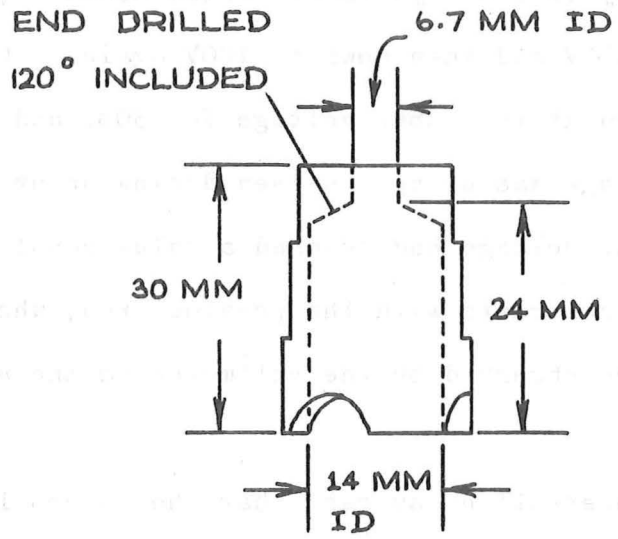


FIGURE 5.27 ENLARGED GRAPHITE EXIT TUBE

variations in composition throughout the arc chamber could contribute to transient easy paths for the arc. The removal of the web beneath each cathode removed the shelter of the cathode tip from the upward flow of hydrogen, and may have caused a further extension of the arc.

From an energy balance over the reactor, the average enthalpy of the carbon-hydrogen stream leaving the exit tube of the reactor was found to be about 150 KJ mol^{-1}. The enthalpy of hydrogen when raised to 10 000K, a temperature in the neighbourhood of those found in hydrogen arcs, is on the other hand about 450 KJ mol^{-1}. If the arc is swept into the small hole which is the exit to the reactor, and which is of about the same diameter as the arc, in order that the arc continue to exist, most of the flow is required to be raised to an ionising temperature. Even when some non-equilibrium is allowed for because of the rapid carrying of ionised matter out through the exit, the energy dissipation required is likely to be above that possible from the arc, and this will be extinguished.

87-92 Fig.5.27 To attempt to avoid the arc being necessarily swept out of the exit tube if and when it extended into the exit tube, the diameter of the upper section of the exit tube was enlargened. The total hydrogen flow was kept at a low value of 10 g h^{-1}, as in the preceding few runs, and current held between 20 and 30 A, as before. The arc stability was somewhat worse under the same conditions as before, with the arc extinguishing more frequently than before, and the voltage rising

to about 160V over 5s to blow out, at times, or operating at 120V to suddenly blow out at other times. The sweeping of the arc through the exit hole as proposed above is not supported by this comparison, and it appears that the proximity of the hot graphite wall of the exit tube lent some stability to the arc.

A hissing noise was heard at the cathode which was used to start the arc, while the cathode was carrying all the current, indicating a violent movement of the arc around the cathode tip. It was noticed again that at low currents (20 A) the anode tip needed to be slightly upstream of the cathodes for stability. In this position a slowly varying voltage in the range 80 to 125V was obtained, and rapid fluctuations from 70 to 150V (over several seconds) and extinguishing of the arc only occurred when the anode tip was opposite the cathodes or below it. One exception to this was found, where the anode had been driven past the cathodes by a distance greater than 5 mm, and the 70-170V fluctuations together with arc-quenching were observed. This behaviour was only observed momentarily after starting (touching a cathode on the side of the anode) and may be cast into the same pattern as all the other observations by noting that the arc attachment is first made on the anode opposite the cathode, and often remains opposite if the anode tip is too far forward. During a period where the voltage was slowly varying between 110 and 125V, a vertical bright orange "flame" only about 0.5 mm in diameter was seen to dance about very rapidly on the projection screen above the anode.

This was taken as the arc attachment on the cathode opposite, since no related movement was seen with the wide attachment on the anode.

To investigate further the apparent effect of the hot exit tube on the arc, the previously used conical exit tube was placed just above a 20 A arc struck in air between graphite electrodes. The arc bowed up inside the vertically held tube more sharply than without the tube, thought to have been caused in part, at least, by the more localised natural convection in the tube. One would expect a longer arc in these circumstances. The arc voltage however decreased from a steady 80V without the exit tube, to a steady 75V when the exit tube was placed over the arc, which burnt normally with its length nearly horizontal. A voltage of 80V was again obtained when the exit tube was lifted away. The arc was observed to follow the tube as the tube was raised, until the tube was about 5 mm above the normal position of the arc, when the arc reverted to its normal free-standing mode. The graphite tube was held lightly by hand with a pair of steel tongs with its largest end downwards, and quickly became white hot when placed over the arc. If one takes an arc with a lower voltage to be the more stable one, this observation corresponds with the observation of less frequent extinguishing of the arc in the reactor when the smaller tube was used. The smaller tube also ran hotter than the larger tube, because of better thermal insulation from the main graphite body.

A hole was cut through the wall of the exit tube in the reactor so that a view could be had of the arc inside.

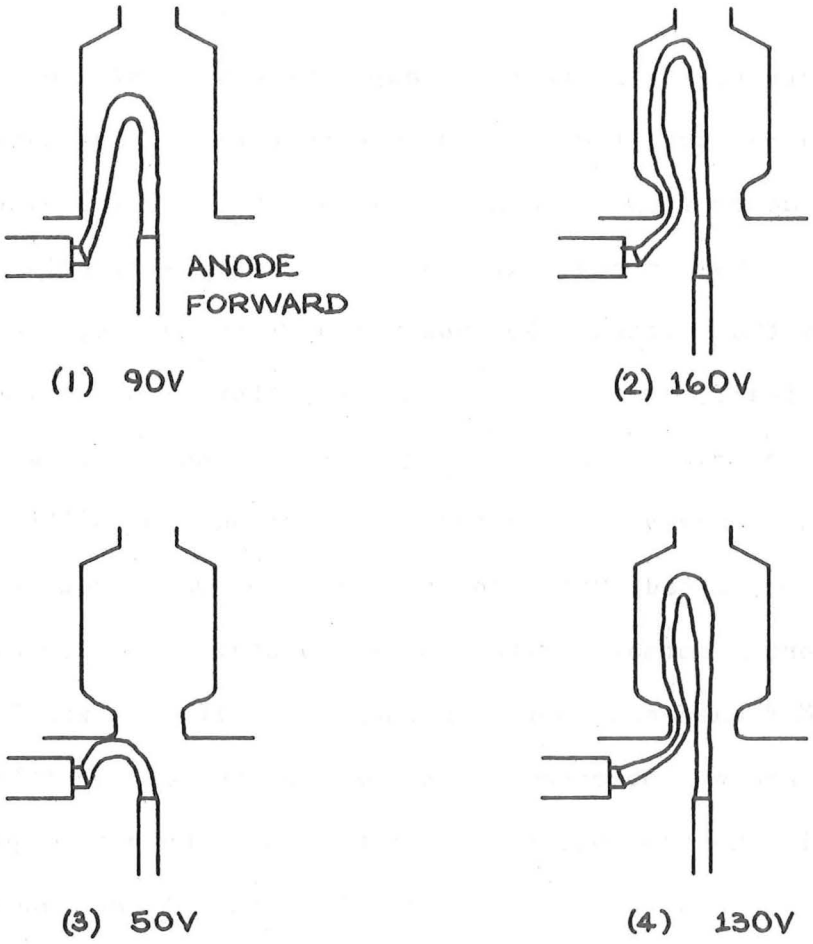


FIGURE 5.28 SUGGESTED ARC BEHAVIOUR
USING: ARC GRADIENT 1·5V MM^{-1}, ANODE DROP 20V,
CATHODE DROP 10V.

For a low current (20 A) the arc was coloured blue just above the anode, and appeared to be alternating between orange and blue within the exit tube.

With the purpose of improving arc stability after a period of 160V excursions from the 90V norm, one cathode was advanced towards the anode from the standard position by about 2 mm. The excursions to 160-170V remained for a short while, but fluctuations of voltage down to 45V from 80V-90V were also noticed, where there were none before. The other two cathodes were brought in to the same extent for a short time, and all brought out to the standard mark again. Periods of running at 45V developed, when the anode tip was opposite the cathodes or below them. Only when the anode was operated well forward, did the voltage suddenly jump to 80-85V and remain there. A voltage significantly higher than 80V was not observed until a cathode which could be seen to have a carbon deposit on it was withdrawn from the reactor chamber. Voltages of 165V were then observed as fluctuations from 105V for a short time, after which voltages of 50V were the only excursions. All the cathodes were then withdrawn by several millimetres, resulting in a stable arc of 100 to 130V. After the run, about 1 mm of deposit was found on all the cathodes, and a large amount of deposit found at the bottom end of the exit tube.

On the assumption that the arc had a uniform voltage gradient of about 1.5 mm^{-1}, (a value calculated from the difference in arc voltage observed in these experiments when an appreciable length of anode fell away), a theory could be

constructed which at first sight accounts for the above observations. All voltage changes are then explained in terms of a change in arc length. This theory is presented in figure 5.28. The theory must be modified slightly to account for the 160 to 170V arcs observed.

A voltage of 170V at 1.5V mm^{-1} with electrode drops totalling 30V requires an arc length of over 90 mm, which seems impossible in the arc chamber itself, and needs the existence of the arc in the quench tube. This has previously been argued to be unlikely. The highest voltage gradient one can safely assume for some parts of the arc is that of a pure hydrogen arc, which is about 4V mm^{-1} (1). It is reasonable to assume a voltage gradient of about 1.5V mm^{-1} for a short distance above the anode, perhaps 10 mm. A potential difference of 170 - 30 - 15 = 125V may be accounted for by an extra arc length of 125/4 = 31 mm, giving a total arc length of 41 mm, which is a manageable length to be contained within the arc chamber.

No good reason is given in this scheme for the apparent discontinuous nature of the transition between the 80-130V regime and the 160V regime. The arc has been observed running steadily at 165V for half a minute, and from 80 to 130V for much longer times, but not continuously at intermediate voltages. A clue is given when one compares the maximum steady voltage obtained with the conical exit tube, about 150V, with that obtained with the enlarged exit tube, about 170V. The internal height of the exit tube was not changed, but both its internal volume and surface area were increased. If the arc lay along

the wall for some reason, or followed it at some distance out, then the length of the arc and thus the voltage would increase or decrease with an increase or decrease of the vertical cross section perimeter of the inside wall. A suitable mechanism will be proposed in a later chapter. It is proposed here that the high voltage operation corresponds to the arc hugging the hot graphite wall, whereas the more variable lower voltage operation (80-130V) corresponds to a free-standing arc.

93-95 The viewing port through which observations were made of the anode, was enlarged horizontally by filing away the graphite wall, so that one of the cathodes could be seen from the side. Some of the arc behaviour was thus observed. For a low current (13 to 17 A) the arc was occasionally seen to jump almost directly across the gap between the cathode in view and the anode, being blue in colour along its length. (See frontispiece) Associated with this short arc was a drop in arc voltage from about 90V to 60V, although this did not always happen with the shortened arc. As the reactor body heated, a very light blue was seen in the space between anode and cathode, even when the arc was elsewhere in the chamber. While the arc was fluctuating between 100V and 55V, indications of varying rates of carbon ablation rate from the anode were found. As the voltage dropped to 55V, the carbon feed was doubled to make up for an increase in carbon loss, and several seconds later the product gas rotameter showed an increase in gas flow of about 50%. The current was increased to 30 A while the chamber was hot, and the blue colour between the cathode and anode became as intense

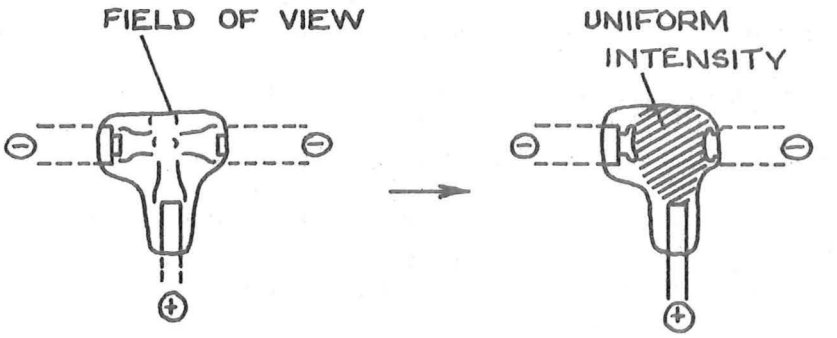


FIGURE 5.29 VIEW OF 35A ARC WITH LOW HYDROGEN FLOW

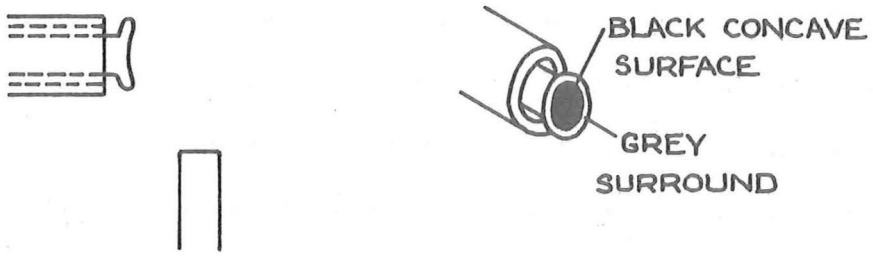


FIGURE 5.30 DETAIL OF CATHODE DEPOSIT

as the arc had appeared before, but was spread over all the region which could be seen. The arc voltage became very stable at 95 to 100V, but slowly decreased over several minutes to 45V. Appreciable carbon deposit was found on the cathodes after the run. Nodules of carbon about 1 mm in diameter were found on the bottom end of the quench tube, which could be easily rubbed off.

Marked differences were observed between runs in the ease of maintaining the arc, and in the rates of depositing on the cathodes. It was noticed with a very low current run, that a small change in the cathode hydrogen flow rate consistently influenced the operating voltage by about 10V, so it was decided to try to relate the cathode flow to the arc stability and carbon deposit. The last 8 runs were compared, and it was found that a cathode hydrogen flow of 0.7 to 0.8 g h^{-1} for currents between 20 and 35 A allowed little carbon deposit, and alleviated blow-out problems. Cathode flows as large as 1.0 g h^{-1} were associated with an unstable arc, even larger flows were associated with rapid deposition,and flows less than 0.7 g h^{-1} resulted in spattering of tungsten from the cathode tips. The following runs were operated with the cathode flows close to the optimum for the particular current used.

96-100 Further gains in viewing the arc chamber were made by filing away the reactor body so that all three cathodes, together with the anode, could be seen through the quartz window. During a run where the total flow of hydrogen was 10 g h^{-1}, and after the reactor body had been heated by the arc running for a period at a low current, the current was set at 35 A.

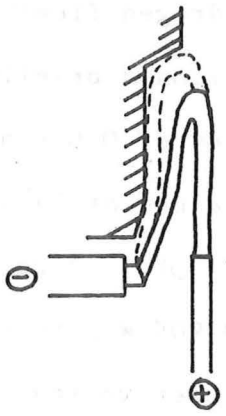
A pronounced "cross" configuration was observed, as shown in figure 5.29, with branches from the two cathodes which were viewed from the side. All the region of the arc chamber in view was a light blue in colour, but the arc branches were especially intense, and were directed horizontally out from each cathode, to meet the vertical stream from the anode in what looked like a turbulent region. A luminous flow continued upstream in line with the anode. Dancing flecks of red were observed about the cathodes. Over a period of about 5 minutes, the voltage of the arc dropped slowly from 95V to 62V, with the current rising from 35 to 39 A. During this time the arc branches gradually became indistinguishable from the surroundings, resulting in a hazy blue throughout, with no red areas observed. Incandescent carbon deposit was noticed on the cathodes by the time the voltage had fallen to 70V, and when the reactor was shut down, about 1 mm of carbon was found deposited on each cathode. This deposit was concave and black towards its centre, and faced the centre of the reactor, as shown in figure 5.30.

The observations described above indicate a change in mechanism of the arc at higher currents from that controlling at lower currents. It may be instructive to compare this run with run 89, where similar conditions were obtained, except that the anode was kept forward of the cathodes when the current was raised. The voltage dropped to 55V immediately, and slowly to 50V over 2 minutes. Over this time, excessive deposit developed on the cathodes. It appears that faster carbon deposition occurred, and a lower arc voltage resulted by allowing a direct arc

to form between cathodes and anode.

Some observations on the relation between the cathode hydrogen flow and arc voltage were made in run 99 for a low current (9-11 A) and a low total hydrogen flow(10 g h^{-1}) which corresponded with those already mentioned briefly in run 92. Run 99 was begun with a hydrogen flow of 0.6 g h^{-1} through each cathode. The arc voltage remained at 115-120V for some time, but then dropped gradually to 85V. A period of sharp changes in voltage between 115V and 90V was then observed, followed by a short period at the lower voltage during which a drop from 85 to 77V was found. It was discovered that the cathode hydrogen flow was 0.7 g h^{-1}, and this was corrected to 0.6 g h^{-1}. The voltage immediately jumped to 110V, around which it fluctuated for the rest of the run. Both the 110-120 and the 75-90V regimes were observed with the anode tip well forward of the cathodes as well as with it opposite them, thus ruling out the possibility of coincidental changes in anode position accounting for the behaviour. The cathodes did not appear to be heated even to a cherry red ($\sim$ 1100K), for they were too dim to see.

These observations can be simply explained in terms of the free-standing/wall hugging proposals. The arc attachment at the cathode would need little gas flow to deflect it and the arc in any direction. A gas flow of 0.7 g h^{-1} (a velocity of 1 ms^{-1} through the annulus at room temperature) may be sufficient to blow the arc in towards the centre, as outlined in figure 5.31, and ensure the stability of a free-standing arc.



——— CATHODE HYDROGEN FLOW 7 g h^{-1}

- - - - - CATHODE HYDROGEN FLOW 6 g h^{-1}

FIGURE 5.31 PROPOSED MODEL FOR 11 A ARC

The alternative arc mode proposed, that laying along the tube wall, may be allowed by the lower cathode flow. This model assumes that the wall mode has the higher voltage, and fits in with the run observations if this assumption holds. However the assumption appears to contradict the lowering of arc voltage when an exit tube was placed over an arc between graphite electrodes in air. This point will be taken up in chapter 7.

101-103 The total hydrogen flow to the reactor was increased from 10 to 18 g h^{-1} for runs 101 to 113. A repeating sequency of events was noticed during a 22 A run. Normal operation consisted of the arc reaching downstream from the anode out of view, and reaching upstream back to the cathode, with an arc voltage of 110 to 120V. Occasionally the arc was seen to jump across the field of view between the electrodes, accompanied by a drop in voltage to 70V and an increase in current. These momentary arcs had a red ending on the cathode. Several alternatives then arose. The arc was either extinguished at the low voltage, or the voltage rose again as the arc disappeared from view. Sometimes the arc voltage steadied at 110V, but more often rose to about 155V. At this point the arc extinguished, or remained steady for several seconds before dropping to 110V again. At one stage, an intense blue-green colour was noticed by looking through the port cut through the wall of the exit tube, just as the arc was extinguished. A strange observation was made when the voltage rose to 155V for sufficient time to make a steady carbon

rate reading. The carbon loss rate increased above the average. This observation had been made in a previous run, and contrasted with other observations at high voltages where the carbon loss was negligible.

Many runs ended with their cathodes looking as though they had been equally used, but the last run ended with two electrodes clean, brown over their lengths, purple near their tips, and slightly melted, and the other a metallic grey. The last was the electrode most prominently in view. A mechanism to explain the sequence above was proposed. As the power supply was attached by the same busbar to all three cathodes, the arc could choose the number of cathodes it attached to, as well as the current distribution between them. Three distinct types of arc seem apparent from experiment. It was proposed that the low voltage arc directly bridging the gap between anode and cathode was attached to one cathode only, the intermediate voltage arc was attached to two cathodes, and the high voltage arc was attached to all three cathodes. The length of the arc, and thus its voltage, would depend on the extent to which it was swept upstream by the gas flow. This in turn would become greater if more of the arc was exposed to the gas flow. Thus the three-branched arc, with only 1/3rd of the total current in each branch, and all branches exposed to convective forces, was very susceptible to being extended, and even swept out the exit tube. The two-branch arc could avoid the centre of the stream and become more stable near the wall at a lower voltage. The single-branch arc was both the strongest in current, and least exposed

to a flow of gas, indicating a short length.

104-105 To test whether the multi-cathode theory described above was necessary to explain the normal operation of the arc at currents below 30 A, two cathodes were removed from the reactor, leaving the cathode which was most exposed to view. Almost all of the time during a 20 A run with the sole cathode, the voltage remained between 90 and 130V, as with the 3-cathode reactor. One excursion rose as high as 150V, just before the arc extinguished, and another dropped as low as 50V. The arc made rapid dashes to the side of the anode, to bridge the electrode-electrode gap more directly, but the voltage was observed not to change significantly from its previous value (120V in one instance). During the 90 to 130V operation, the arc attached squarely on the end of the anode as in previous runs, and a rapidly quivering orange plume was seen as the arc attachment at the cathode, located on the top of the cathode tip.

Similar behaviour to the above was observed with a current of 33 A. The arc extended directly forward from the anode, with a running voltage of about 100V. Although these observations cannot disprove the operation of the multi-cathode mechanism proposed above, they at least show it not to be a necessary explanation of 3-cathode operation.

106-113 The other two cathodes were replaced, and the 3-cathode assembly used for the remaining runs. It was noticed after one extended 70V run where extensive carbon deposit formed on the cathodes, that the exit tube had no noticeable deposit on

its walls.

A careful look was taken at a 40 A arc just after starting. Within half a second of withdrawing the cathode used to start the arc, it could be seen that the arc had transferred also to the other two cathodes. An effect on arc behaviour of the increase in total hydrogen flow from 10 to 18 g h^{-1} was seen. With the higher hydrogen flow, the arc operated well forward, (that is in the low current mode) with a current of 40 A, and assumed the "cross" configuration when a current of 45 A was used (frontispiece). This can be compared with 30 A and 35 A for the low current and high current modes respectively with the lower hydrogen flow of 10 g h^{-1}. It is thus reasonable to suppose that the transition point between modes depends on a balance between the forced convection forces and some natural forces of the arc itself. It was found that the cathodes were clean after an extended period of operation with the low current mode, but appreciable deposits formed on them with the high current mode, with only 8% more current being used. The same cathode flow was used in both cases in the comparison.

114-117 The total hydrogen flow was increased again, to 28 g h^{-1} for these last runs. Running in the low current mode at about 33 A, the arc had a voltage which varied from 95 to 120V and was no higher than that experienced for 30 A previously with the much lower hydrogen flow 10 g h^{-1}. Thus the low current mode of arc operation appears not to be influenced by the range of forced convection velocities used. However, much less was seen of the

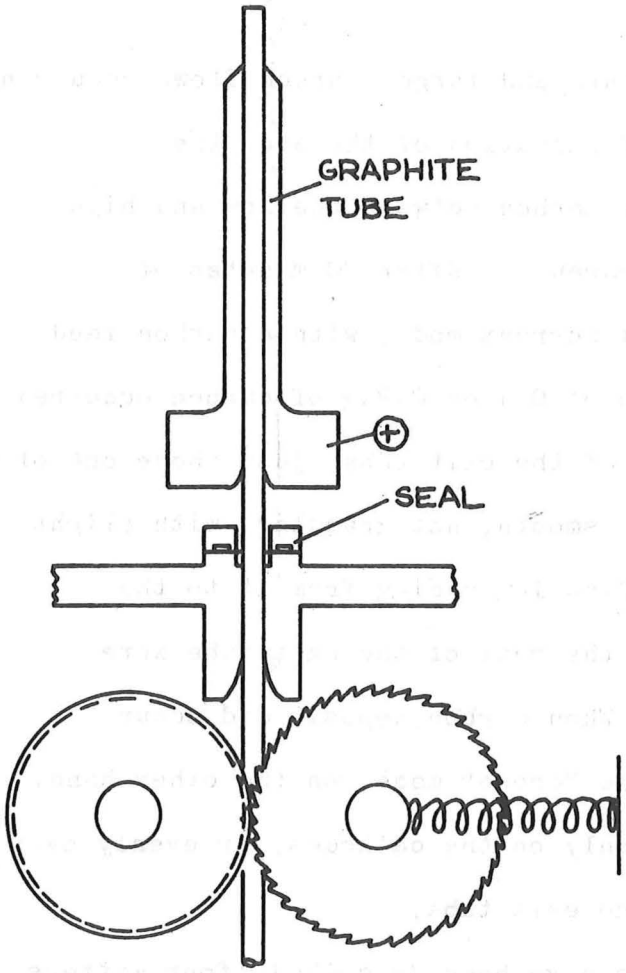
arc jumping directly across to the cathode than with the lower hydrogen flows.

With the higher currents and larger carbon flows occurring in the "low current" mode of operation of the arc, the differences in deposition of carbon between the low and high current mode became more apparent. After 20 minutes of operation at 33 A in the low current mode, with a carbon feed rate of 27 g h^{-1}, a build-up of 0.1 or 0.2 g of carbon occurred low down on the inside wall of the exit tube, just above one of the cathodes. This deposit was smooth, not granular, with slight markings on its surface, indicating arcing from it to the cathode. The cathodes and the rest of the exit tube were almost free from deposit. When carbon deposit did occur with the arc operating in the "cross" mode, on the other hand, significant deposit formed only on the cathodes, or evenly over all the inside surface of the exit tube.

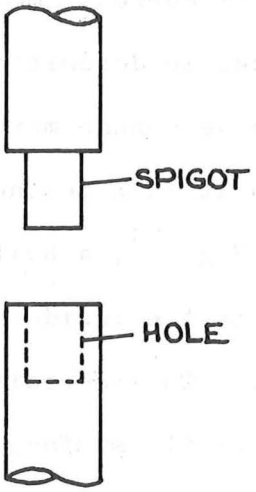
Now that all the runs have been described, four matters deserve separate mention.

(a) Anode drive and electrical contact

The original design of carbon feed is shown in figure 5.31. A graphite tube was used to contact the graphite rods from the power supply. The preceding rod was prevented from falling off the following one, and was electrically contacted to it by a spigot-hole join. A rather flexible coupling of polythene tubing was made from the drive shaft of the motor-gearbox to the rubber drive wheel.



(A) ORIGINAL FEED SYSTEM



(B) ANODE ROD
JOIN

FIGURE 5.31

The graphite tube was found to be too fragile for repeated assembly of the reactor, although it served its purpose well in other respects. It was replaced by a tungsten rod, drilled down its centre so that contact could be made with the graphite rods for a length of 10 mm from the forward tip. It was found too difficult to drill further than 10 mm with a standard 4 mm diameter tungsten carbide tipped drill ground down to 0.1 mm larger than the graphite rods, so the rest of the tungsten tube was drilled to 4 mm diameter, and operated with a coiled nichrome wire inside the hole to contact the graphite rods. With both the graphite and tungsten contact tubes, difficulty was found in feeding when the remainder of a rod was about to leave the tube and electrical contact relied on the rod-to-rod join. At this stage, the feed commonly jammed, and arcing appeared to have caused deposits on the inside of the tube. The tube-to-rod contact could have been improved. It was thought that the sliding contact may have been so poor that almost all the current was passing through the brass follower wheel to the graphite rod. This was indicated by the heated sticky appearance of the rubber of the rod seal after a 60 A run. Efforts to improve the feed were however directed at the rod-to-rod join.

A holder was made up to hold two rods together in line, and to pass a direct current from one rod to the other. Several joins were tested of different designs, with an end thrust which was unavoidably larger than that experienced in the reactor. The plain spigot-hole join was found to have a

0.14 Ω contact resistance, (cf. 0.35 Ω for 300 mm of the graphite rod) and began to glow at the join when the current was just above 20 A. For comparison, a continuous rod over the same test length (50 mm in air between firm cool contacts) showed a dull cherry red only when 60 A had been reached. A copper plating was deposited on both the spigot and inside the hole and the copper surfaces were smoothed. A lower resistance of 0.08 Ω was found, which remained cool up to 50 A. The copper joins proved difficult to fit together in the feeder, and mechanical action disturbed them making them no better than the graphite spigot-hole join. Conical joins were then made from the ends of the rods. A 30° included conical join glowed a bright red at 60 A in the test rig, but was considered satisfactory.

In the reactor, a successful change-over from one rod to the following one was made with an arc of 52 A, using the conical join. It was easily unseated, so a deeper conical join was made, using a cone of 20° included angle. This was found satisfactory for the rest of the runs, provided care was taken to keep the surfaces concentric with the rod, and to rub in by hand the matching surfaces before they were used. All rods were also smoothed by emery paper beforehand so that they fitted through a suitable hole gauge, and did not cause any sticking in the reactor feed hole.

(b) Shape of the anode tip

Four distinguishable shapes of the anode tip were observed, as drawn in figure 5.32. At low currents, the arc "burned" squarely on the end, and had a definite jagged edge, somewhat like

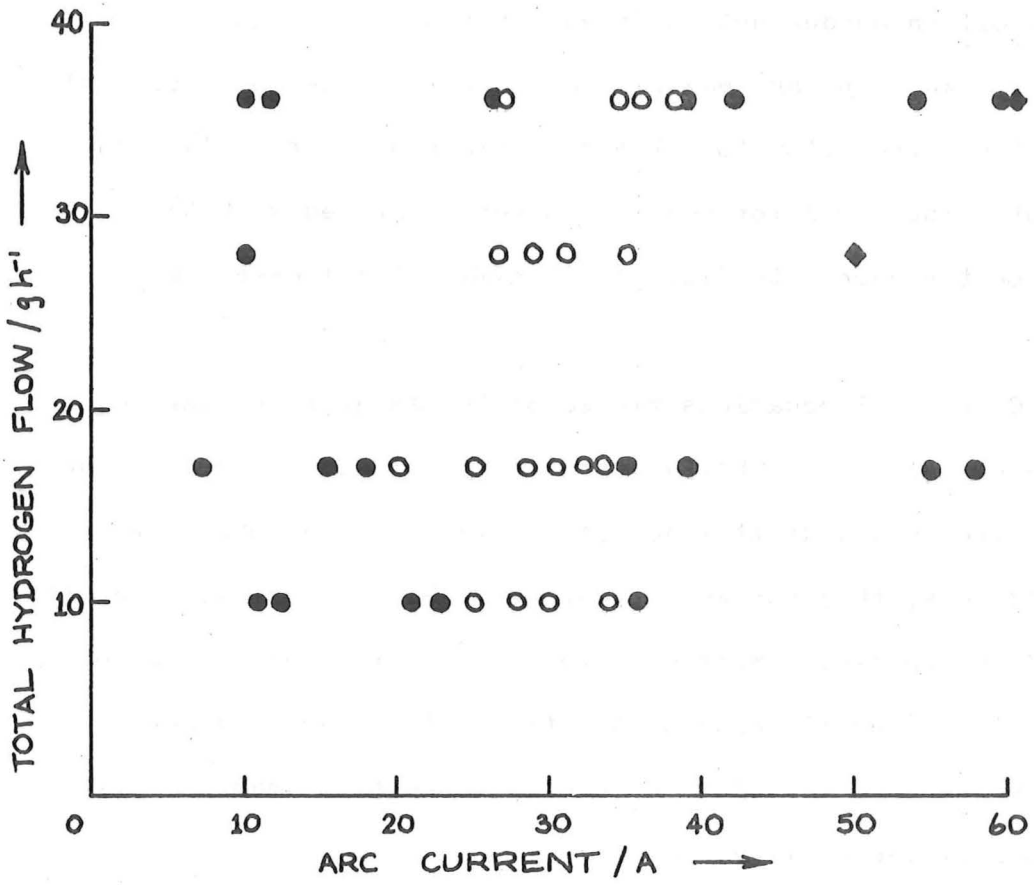
the edge of torn paper. With larger currents, the apparent steadiness of the carbon ablation rate was gone, even with a constant current and voltage. Observations were made of several aspects of this unsteadiness.

(1) Pieces up to 6 mm long would appear to break off from the anode, associated with a rise in arc voltage as high as 10V. However, no solid pieces of rod were ever found on the reactor floor or in the gas cooling section unless a piece was observed to fall off an anode-anode join and thus stop the run. The pieces would break away regularly so that the operator could adjust the carbon flow to allow for this behaviour. When the rates of carbon feed for these runs were compared with those for which the tip burnt steadily, no significant difference was found.

(2) On several occasions pieces of the anode were observed to come off slowly. They appeared to partly separate from the rest of the anode, drift sideways slowly and float off. While they did this, they changed colour from white to brown. In all the runs where pieces were observed coming off, thin leaves of carbon were found littered on the floor of the arc chamber or stuck between the cathodes, or blocking the exit chamber, or on the floor of the cooling chamber.

(3) After one run, a paper-thin tubular wall was found standing above the anode about 4 mm, as a continuation of the outside surface of the solid anode rod. This tube was very fragile, and was a grey colour. It looked to be of similar material to the leaves found on the chamber floor.

FIGURE 5.32 ANODE TIP SHAPE AS A FUNCTION OF CURRENT AND TOTAL HYDROGEN FLOW



As all the observations (1) to (3) occurred in the same hydrogen flow - current region (see figure 5.32), it was assumed that they all belonged to the same phenomenon. Further discussion will be presented in chapter 7.

It can be seen from figure 5.32 that for currents above a certain value, depending on the hydrogen flow, the tip of the anode appeared open again. Either a pointed shape appeared, or the tip showed a roughly square end. Not sufficient information was gained in the experiments to characterize when these alternatives appeared, although they alternated during a 60 A run. It was noted during two runs at an intermediate hydrogen flow that this "square" end was a distinctly rounded "blob".

(c) Tungsten Movements

If the tungsten tip appeared clean of deposit, and melted after a run, a metallic-looking substance was sometimes found either between and above the cathodes on the lower inside surface of the exit tube, or lying as a solid "pool" 1 to 2 mm across in the crater of the anode tip. When the deposit was found on the exit tube, it occurred either as small drops or as a continuous layer. The deposit was shiny, had a slight gold tinge on its surface. It was thought to be tungsten. It was surprising that no trace of this material was found on the chamber floor, on the anode assembly, or elsewhere in the reactor chamber.

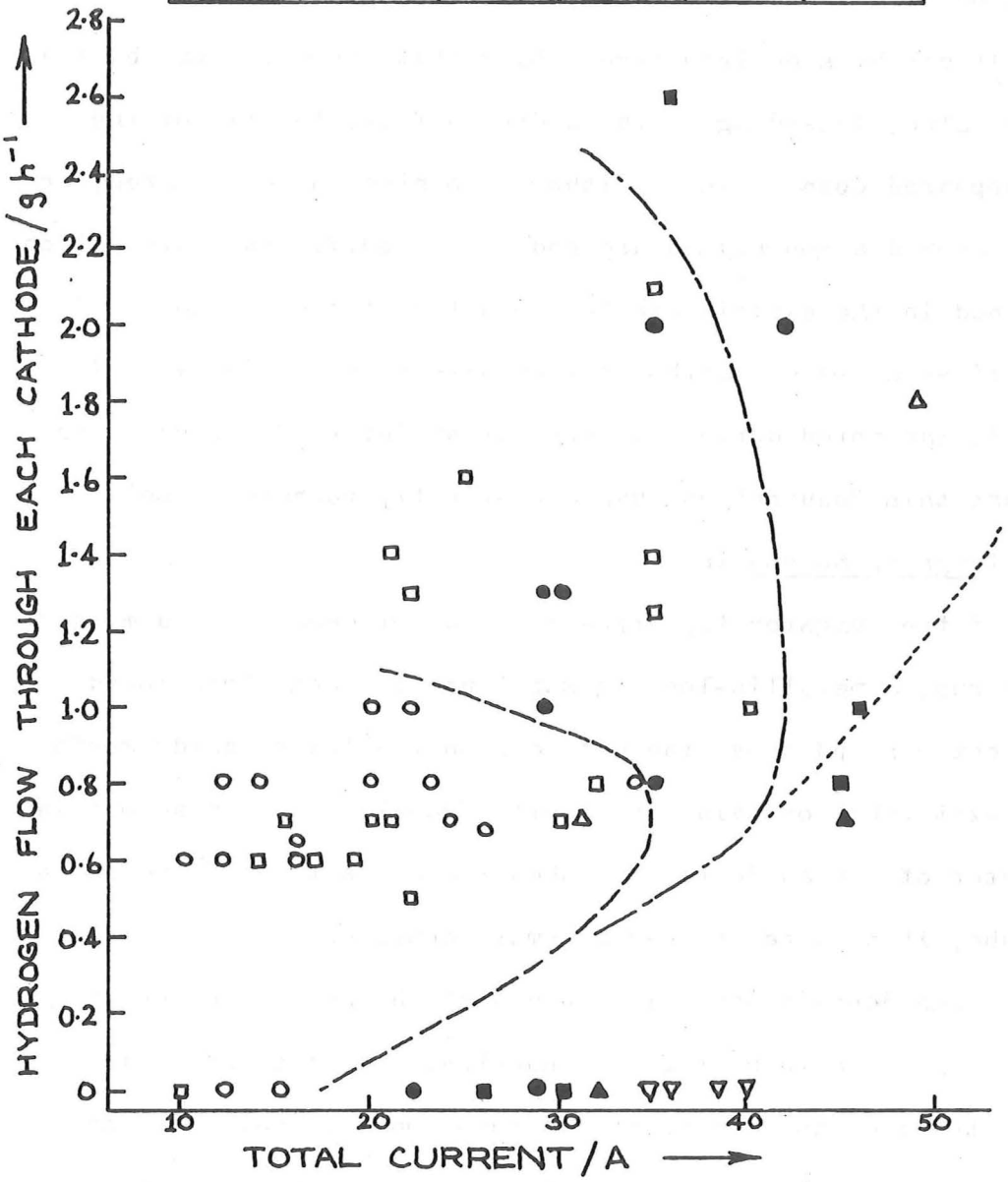
(d) Carbon Formation on Cathodes

To summarise the operating experience with the solid 3.3 mm diameter cathode tip, a chart was made out showing the three independent variables, current, total hydrogen flow rate, and the

FIGURE 5.33 CARBON BUILD-UP ON SOLID TIP

3·3 MM DIAMETER CATHODES

HYDROGEN TO REACTOR / g h^{-1}	10	18	28	36
"CLEAN" RUNS	○	□	△	▽
"DIRTY" RUNS	●	■	▲	



flow rate of hydrogen through each cathode tube. An arbitrary criterion of cathode build-up was chosen in order to classify runs as either "dirty" or "clean" cathode runs. The criterion for a "clean" cathode run was that less than 1 mm deposit was observed after 5 minutes of operation at the conditions shown on the chart (figure 5.33). When the runs were divided up in this manner, it can be seen from figure 5.33 that cleaner cathodes resulted from combinations of total current and cathode hydrogen flow lying within certain limits, which broadened as the total hydrogen flow supplied to the reactor was increased. The runs using tungsten rods standing bare, without a surrounding tube, were also included in figure 5.33 as runs with no cathode hydrogen flow. It should be noted that a better thermal contact of the tip with the cooler end of the cathode, was obtained for these runs. Four runs operated with the highest total hydrogen flow used, 36 g h^{-1}, showed less carbon build-up than other runs with lower hydrogen flows. It seems significant that in order that the two runs operated with only one cathode be fitted in with the behaviour of the three-cathode runs, the <u>total</u> current needed to be considered as the important variable, and not the current per cathode.

A certain regularity was observed in the forming of a deposit on the cathode tip. After a period of running under carboning conditions some slight covering of carbon was all that was found on the cathodes. If this covering was not cleaned off the cathode, and the reactor operated again under carboning conditions as shown on figure 5.33, the arc voltage dropped and a massive build-up occurred quickly.

References Chapter 5

1. Maecker, H. "Der elektrische Lichtbogen" Ergebnisse der exakten Naturwissenschaften 15 (1951) 293-358.

2. Li, K.C. and Wang, C.Y. "Tungsten" Reinhold 1947.

RESULTS - QUANTITATIVE

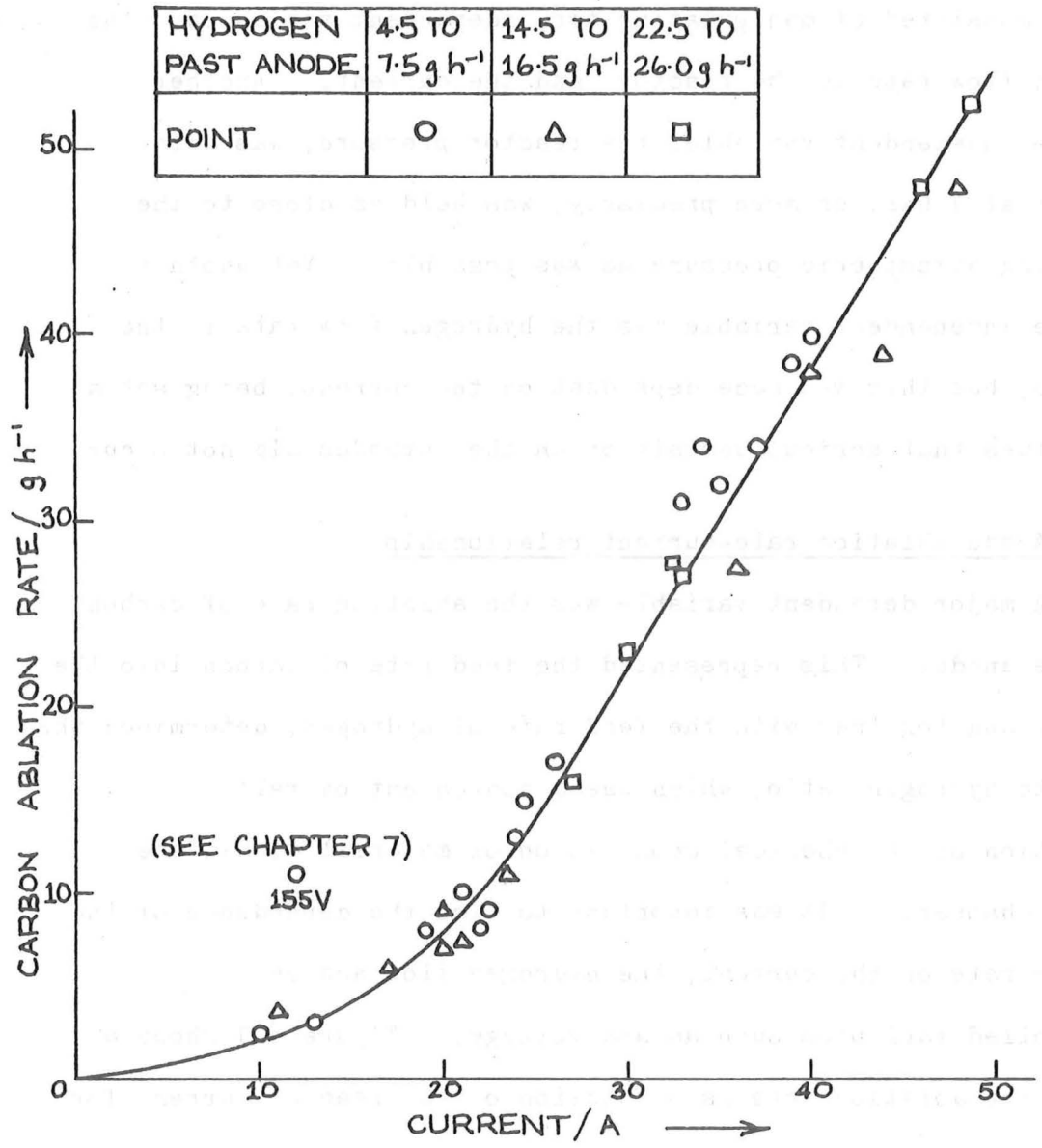
CHAPTER 6

Once the design had been settled, operation of the reactor largely consisted of manipulating two independent variables; the hydrogen flow rate to the reactor, and the current. Another possible independent variable, the reactor pressure, was held constant at 1 bar, or more precisely, was held as close to the prevailing atmospheric pressure as was possible. Yet another possible independent variable was the hydrogen flow rate to the cathodes, but this was made dependent on the current, being set at such values that serious deposition on the cathodes did not occur.

6.1 Anode ablation rate-current relationship

A major dependent variable was the ablation rate of carbon from the anode. This represented the feed rate of carbon into the reactor, and together with the feed rate of hydrogen, determined the carbon to hydrogen ratio, which was a convenient overall description of the chemical composition of material within the reactor chamber. It was important to find the dependence of the ablation rate on the current, the hydrogen flow and on uncontrolled variables such as arc voltage. Figure 6.1 shows a plot of the ablation rate as a function of the reactor current for three different total hydrogen flows. The experimental points shown were chosen for their reliability, from the large number of readings of both current and carbon feed control settings transcribed to paper in consecutive form. All records of the type "carbon rate reading 1; current reading 1; carbon rate

FIGURE 6.1 CARBON ABLATION RATES FROM A 3·3 MM DIAMETER GRAPHITE ANODE AS A FUNCTION OF CURRENT



reading 2; current reading 2" where both readings 1 and 2 were the same, have been placed on figure 6.1. Data has been used which was taken near the beginning of a run, before the reactor walls reached steady state temperatures, as well as during completely steady-state periods, and also from the final moments of a run where fast depositing on the cathodes was observed. Arc voltages varied from 50V to 130V, with one point at 155V. With the exception of the point at 155V, which was observed twice, it can be seen that the behaviour can be reasonably described by a single line.

6.2 Acetylene concentration - C/H ratio relationship

For any given hydrogen flow, it has been shown above that a determination of the acetylene concentration-current relationship also gives the relationship between acetylene concentration and the carbon to hydrogen ratio. It was decided to present the data as a function of this ratio, since any differences observed between concentrations for a given C/H ratio could be attributed to factors influencing the extent of reaction.

Acetylene concentrations were measured using both the gas bubbling trains and the gas chromatograph. The gas chromatograph analysis gave two values, depending on whether the peak areas or peak heights were taken. The analysis by peak area (weight of the paper in the peak) gave values consistently below that given by the chemical method, whereas a measurement of peak heights on the chromatogram gave values on average the same as those by the chemical method, but with a $\pm$ 10% scatter. The chemical method

gave a scatter of ± 0.5% for 100% acetylene standardization samples, and could be expected to give a scatter of about ± 2% for the normal concentrations found. Since much of the ± 10% scatter was attributed to doubts about the position of the acetylene peak baseline caused by overlapping of the hydrogen and acetylene peaks, and since eradication of this uncertainty probably meant the rebuilding of the columns and flow passages in the chromatograph to lessen diffusion of the sample, the chromatograph was not persevered with, and only occasional checks were made with it. However, with the chemical method, occasionally much of the sample was lost through one of the glass joints in the bubbler train. Since the chromatograph results showed no other species than hydrogen and acetylene, even with a limit of detection of 0.1 mol %, the "washing" bubblers were bypassed, and the sample fed directly to the silver nitrate solution. This procedure was used for all the data quoted here as being rigorous.

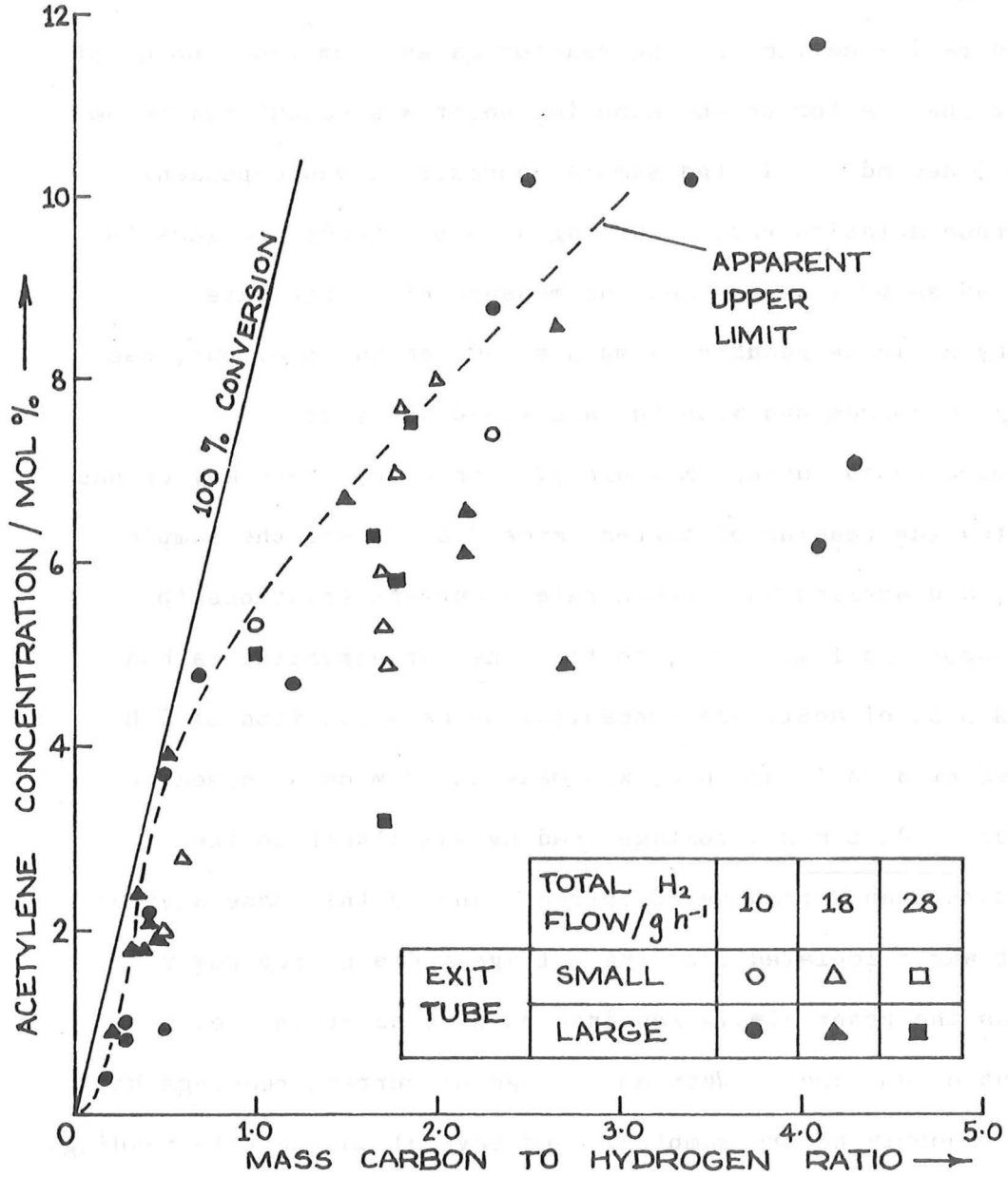
In an initial attempt to calculate the carbon to hydrogen flow ratio appropriate for each gas sample, the carbon feed reading taken nearest in time to the gas loop sample was used. This procedure resulted in a collection of points with so much scatter that only the general area of the variables was indicated, with some suggestion of trends. The scatter was an order of magnitude larger than the likely error of acetylene analysis, and as the hydrogen flow could be measured with as much accuracy, the blame was placed on the measurement of carbon rate. It was noticed during much of the operation that the carbon feed rate

needed to be changed frequently because of changing current, and possibly because of operator error in controlling the position of the ablating tip.

The residence time of the reactor gases from their point of entry into the reactor to the sampling point was calculated to be from 3 to 5 seconds. If the sample composition was dependent on the carbon ablation rate occurring 3 to 5 seconds previous to sampling, as seems likely, then the measure of carbon rate obtained by a single reading as much as 30 seconds previous, was not likely to correspond with the acetylene analysis.

A more instantaneous measure of carbon feed rate may be had if one noted the reading of current made just before the sample was taken, and applied the carbon rate - current relationship presented above in figure 6.1, to find the corresponding carbon rate. A plot of acetylene concentration as a function of C/H ratio, presented in figure 6.2, was made up from data chosen in this manner. At times a voltage reading was closer to the sampling time than a reading of current, and in this case a value of current was calculated from the voltage and a nearby power reading, as the power always remained much steadier than either the current or voltage. When no voltage or current readings had been noted shortly before sampling, and several carbon rate readings were taken before and after sampling indicating a steady carbon rate, this measure of carbon rate was used. For all data not meeting the above criteria, acetylene analyses were rejected as being poorly documented. No sample was taken sooner than 2 minutes after starting the arc, and most frequently was taken

FIGURE 6·2 ACETYLENE CONCENTRATION IN REACTOR OFF-GAS

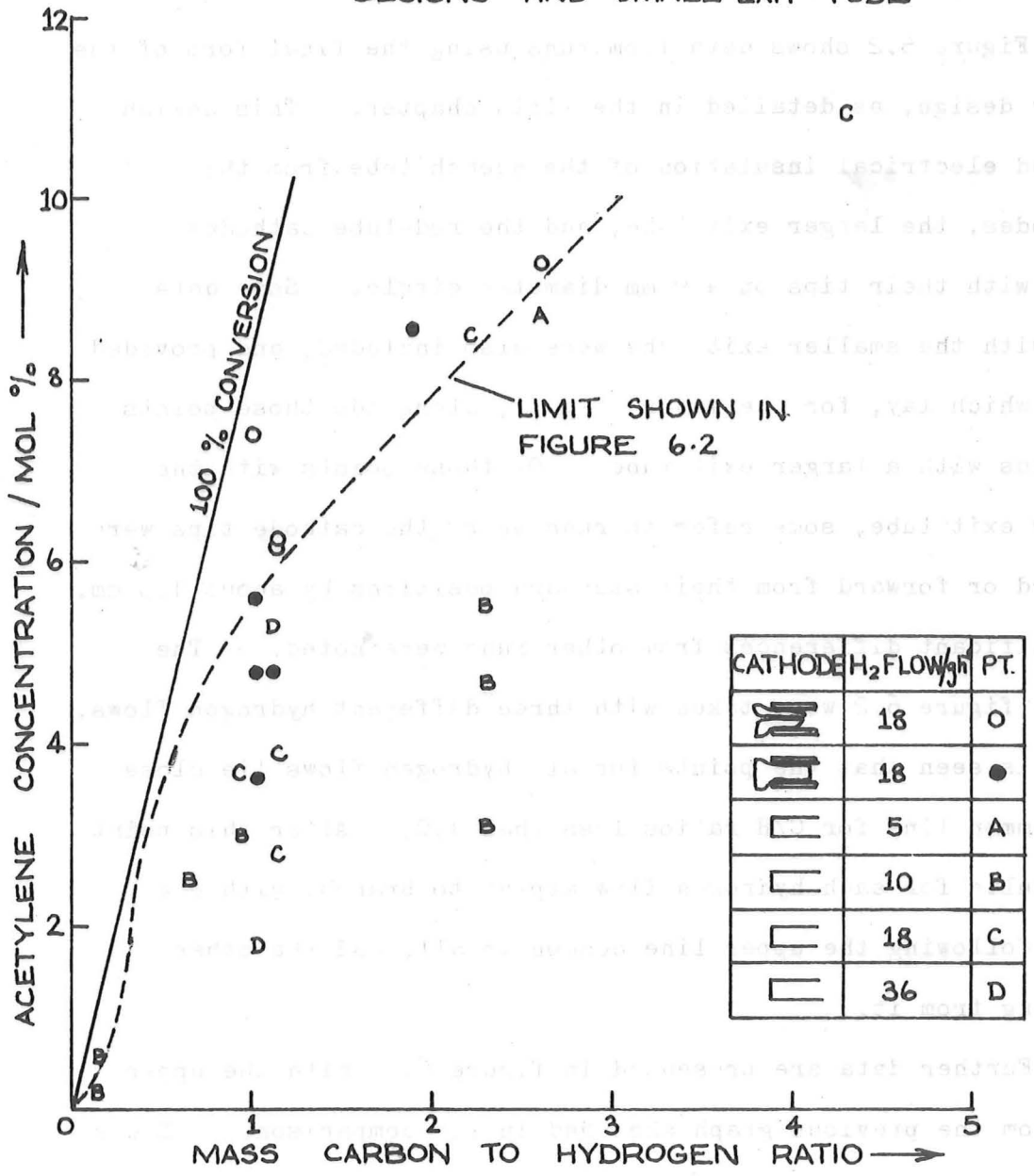


after 5 minutes. No other restriction was placed on the taking of samples, except that they were 1 minute or more apart to flush out the sampling loop and distributor adequately.

Figure 6.2 shows data from runs using the final form of the reactor design, as detailed in the fifth chapter. This design included electrical insulation of the quench tube from the electrodes, the larger exit tube, and the rod-tube cathodes, placed with their tips on a 9 mm diameter circle. Some data taken with the smaller exit tube were also included, and provided points which lay, for the major part, alongside those points from runs with a larger exit tube. Of those points with the smaller exit tube, some refer to runs where the cathode tips were backward or forward from their standard positions by about 1.5 mm. No significant differences from other runs were noted. The data in figure 6.2 were taken with three different hydrogen flows, and it is seen that the points for all hydrogen flows lie close to a common line for C/H ratios less than 1.0. After this point the results for each hydrogen flow appear to branch, with one branch following the upper line common to all, and the other diverging from it.

Further data are presented in figure 6.3, with the upper line from the previous graph sketched in for comparison. These data were taken from runs using earlier variants of cathode design. Those data with insert-tube cathodes were as carefully chosen as the data presented previously, but were non-standard to the extent that the cathode hydrogen flows were not balanced, and no standard position for the cathode tips was used. The data for exposed

FIGURE 6·3 ACETYLENE CONCENTRATIONS IN REACTOR OFF-GAS WITH DIFFERENT CATHODE DESIGNS AND SMALL EXIT TUBE



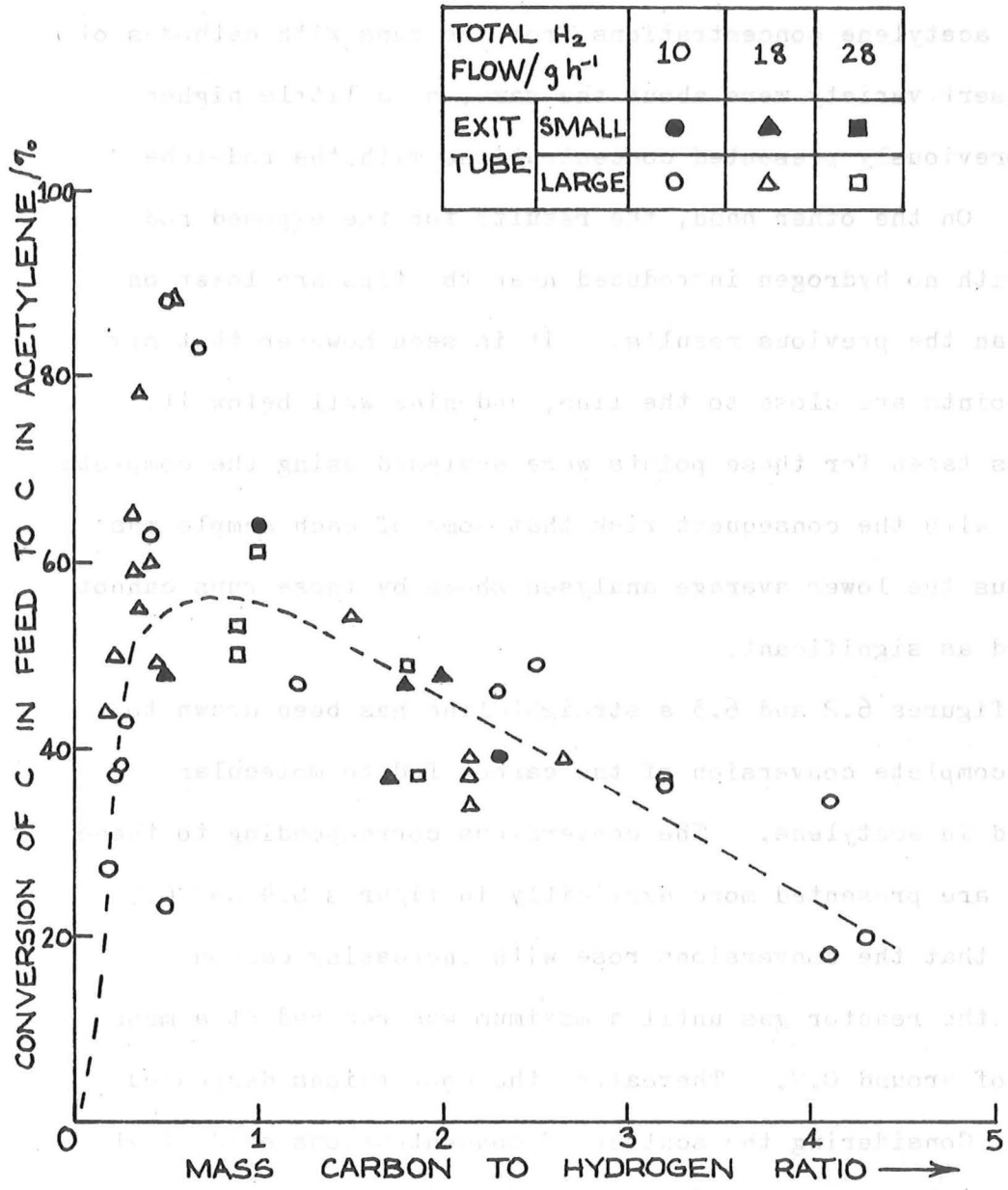
rod cathodes have the same disadvantages, but also could not be checked for reliability, as no detailed step-by-step account of the experiments was kept.

The acetylene concentrations from the runs with cathodes of the tip-insert variety were about the same, or a little higher than the previously presented concentrations with the rod-tube cathodes. On the other hand, the results for the exposed rod cathodes with no hydrogen introduced near the tips are lower on average than the previous results. It is seen however that six of these points are close to the line, and nine well below it. Gas samples taken for these points were analysed using the complete gas train, with the consequent risk that some of each sample was lost. Thus the lower average analyses shown by these runs cannot be regarded as significant.

In figures 6.2 and 6.3 a straight line has been drawn to represent complete conversion of the carbon fed to molecular carbon held in acetylene. The conversions corresponding to these two graphs are presented more explicitly in figures 6.4 and 6.5. It is seen that the conversions rose with increasing carbon content of the reactor gas until a maximum was reached at a mass C/H ratio of around 0.7. Thereafter the conversions decreased steadily. Considering the scatter of concentrations evident at higher C/H ratios in figure 6.2, the 85% maximum conversion indicated by the data may not be trustworthy. A figure of 60% appears more likely, and is indicated by the curve drawn through the points.

The power use for production of a unit mass of acetylene

FIGURE 6.4 CARBON CONVERSION TO ACETYLENE USING SOLID-TIP CATHODES



is shown in figure 6.6. It is seen that the power required dropped as the C/H ratio was increased, reaching a steady value or shallow minimum at a mass C/H ratio of 2.5. Some evidence is seen for a decrease in power requirements with an increase in hydrogen flow. The lowest power requirement (130 kwh kg^{-1}), can be compared with what would be acceptable commercially (11 kwh kg^{-1}).

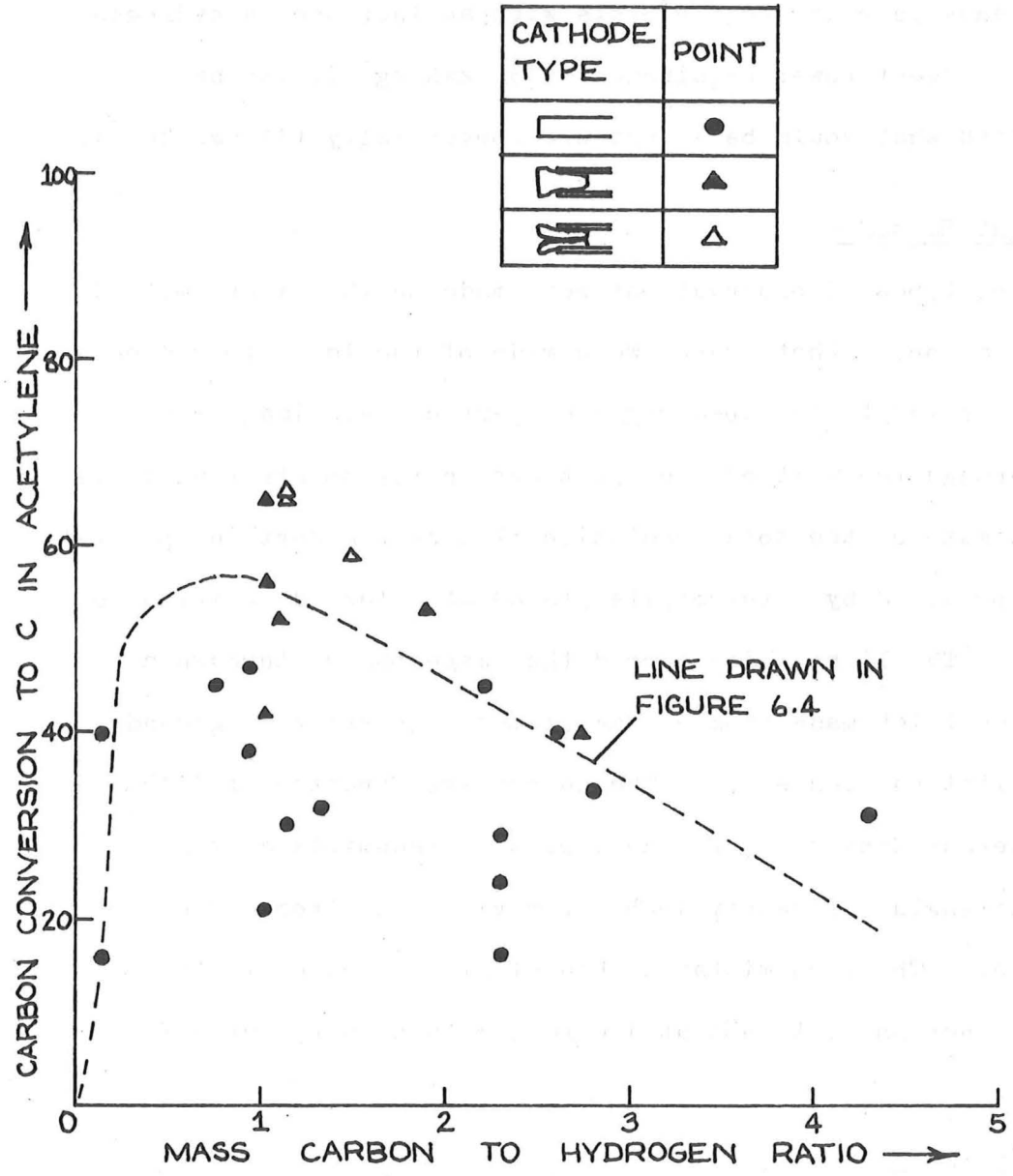
6.3 Light Emission

Three types of observations were made on the light emitted from the reactor. Photographs were made of the image formed on a white plate fixed to the spectrograph, part of this image was allowed through the slit of the spectrograph for spectral analysis, and an estimate of the total radiation flux over a certain spectral range was provided by a thermopile placed at selected positions on the image. The light which formed the image passed through a window 10 mm thick made from 3.3 mm diameter quartz rod, ground optically flat on each end. The quartz was "Spectrosil 'A'" made by Thermal Syndicate, England, with a transmittance for a 10 mm path length of nearly 100% for wavelengths from 220 nm to the visible. The transmittance then slowly decreased as the wavelength increased, to 98% at 1.0 μm, with a sharp cut-off above 2.0 μm.

Spectral Analysis

The spectral analysis will be discussed first. Quartz components were used in the spectrograph throughout, but since they were made in 1937 their transmission was likely to be more restricted in wavelength range than that of the window in the reactor.

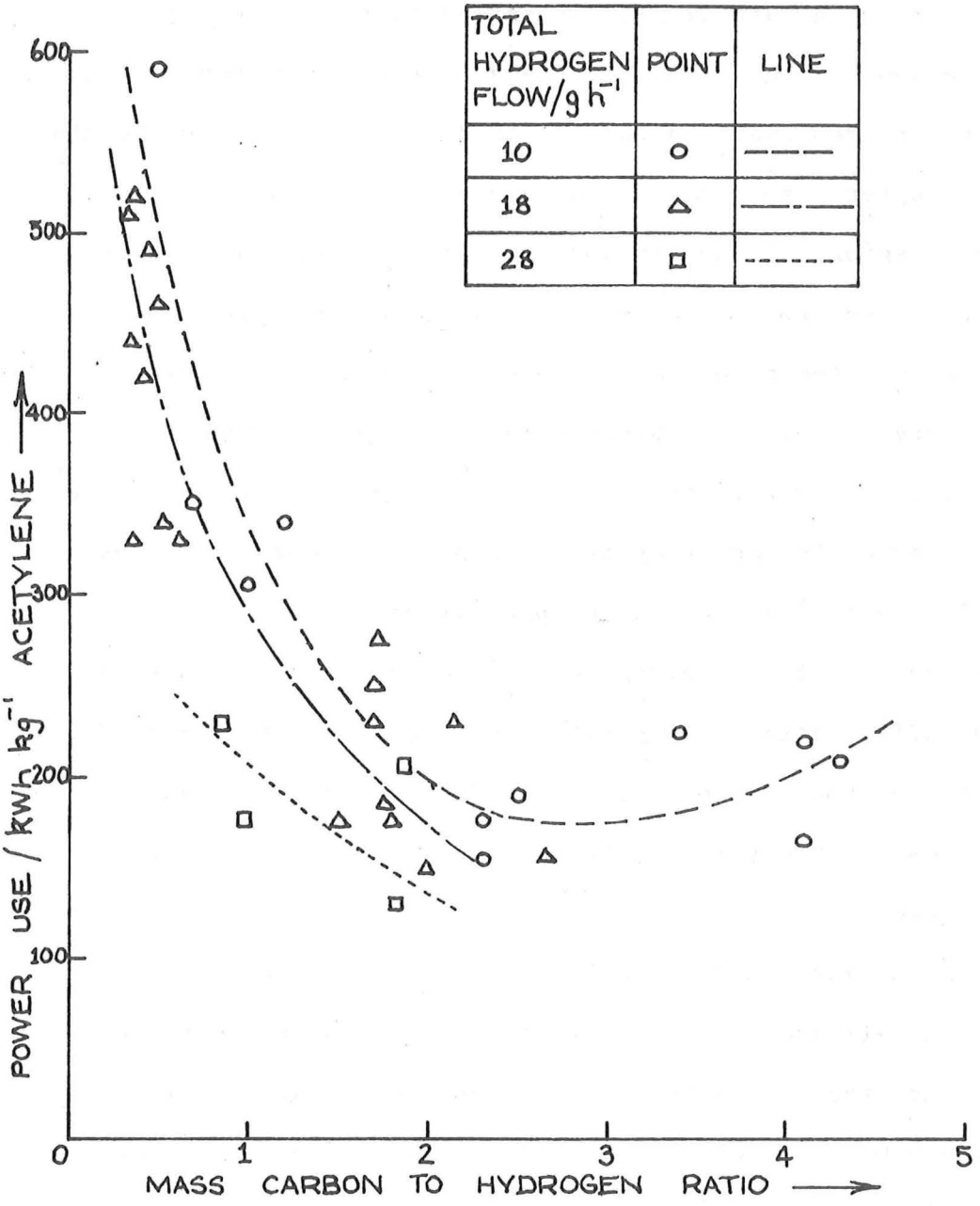
FIGURE 6.5 CARBON CONVERSION TO ACETYLENE USING DIFFERENT CATHODE TIPS

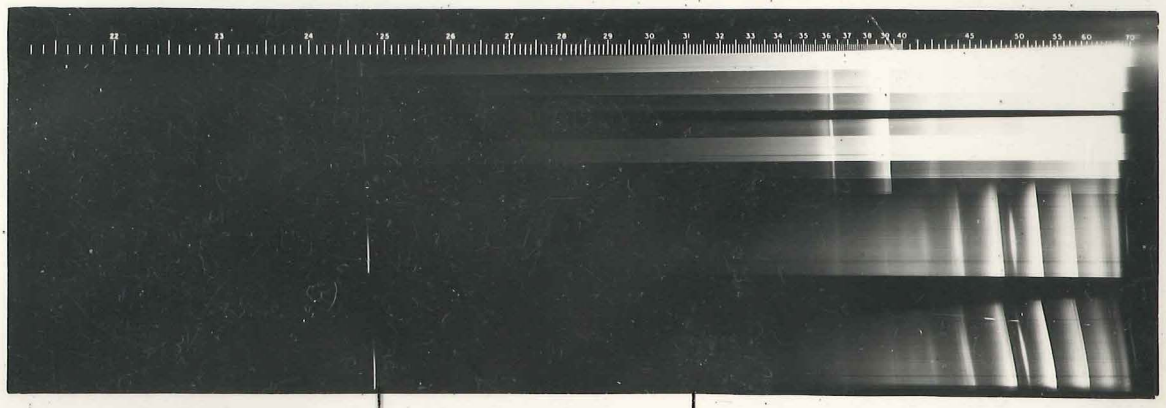


The area viewed by the spectrograph was the very thin strip of the focussed image which lay between the jaws of the slit. The slit was placed across the arc image, corresponding to 0.5 to 1.5 mm out from the anode tipe. An advantage of the prism spectrograph was that the arc was resolved across its diameter along the breadth of the spectrograph exposure. Thus the spectral characteristics of different regions of the arc could be picked out. From this radiation observed from the side of the arc, the true emission from each volume element of the arc may be calculated assuming radial symmetry and optical thinness, and a computer program was developed by the author to solve the Abel integral involved in the problem. However the accuracy of the experimental work did not warrant this sophistication, so the program was not used. The wavelength scale on the spectrograph was out of position, but was calibrated sufficiently closely with radiation from the sodium D lines, from the atomic carbon line at 247.8 nm, and from the prominent atomic mercury lines, to be able to identify spectra from the reactor.

The slit width on the spectrograph was varied to determine the width that allowed the spectral detail to be picked out, but did not distort the peak intensity of a spectral line. With small slit widths good definition can be obtained, with however some distortion of the line intensity profile, and loss of intensity at the peak of the line. With large slit widths, the line intensity profile becomes more rectangular, with the radiation intensity all across the line practically 100% of the true value (assuming no Stark broadening of the line radiation etc.). Large slit widths also produce wide spectral images,

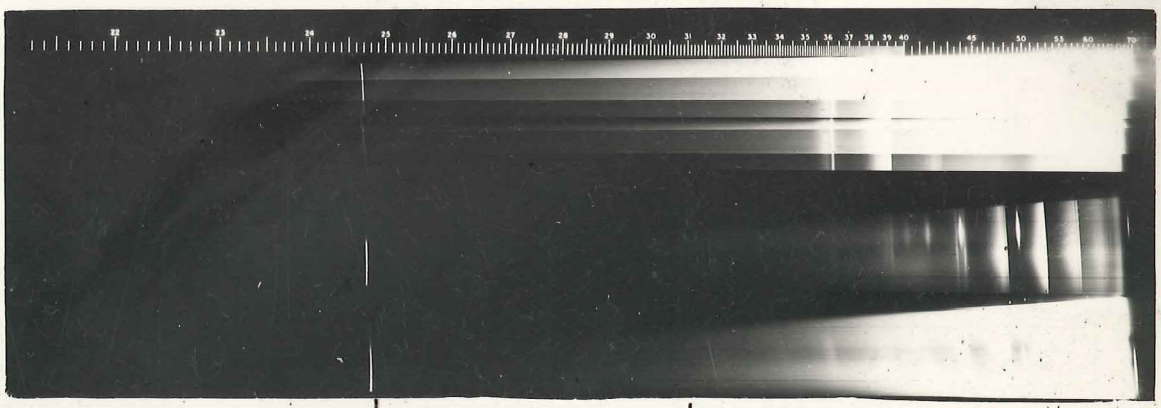
FIGURE 6.6 ENERGY USE FOR ACETYLENE PRODUCTION IN REACTOR WITH 3·3MM D ANODE





CALIBRATION | 22A, 0·02s | 34A, 0·02s

ANODE HYDROGEN 9 g h^{-1} | 6·5 g h^{-1}



CALIBRATION | 17–18A, 0·1s | 24A, 0·1s

HYDROGEN PAST ANODE 28 g h^{-1}

PLATE 6·1 SPECTROGRAPHS FROM A CARBON ARC IN HYDROGEN

tending to merge when the details are close together.
A compromise slit width of 32μm was chosen for this work, as it resulted in smoothly rounded peaks with sufficient separation of detail. The slit width was made dimensionless to check it against other experience. If b = slit width,

λ = wavelength,

and f = spectrograph focal length/lens diameter, the ratio $b/\lambda f$ determines how closely the resolved peak intensity approaches the correct value. For a wavelength of 250 nm, $b/\lambda f = 17$, giving close to a 100% approach (3) and for a wavelength at the other end of the scale, 700 nm, $b/\lambda f = 6$, giving a 97% approach.

Plate 6.1 shows two spectrograph prints. Each print has the wavelength scale exposed on to it, and also a calibration set of six blackbody exposures. The six different blackbody "intensities" were all obtained from the same radiation source, but exposed for different times, and with a diaphragm to cut down the intensity. The positive electrode of a quiet carbon arc was used as a radiating surface at an effective blackbody temperature near 3800K (1,2) as outlined in chapter 4. Exposure times of 0.02, 0.1 and 0.5 s were used, in conjunction with no diaphragm and with the diaphragm in place, to obtain the six densities of exposure. Two exposures of the reactor arc are also shown on each spectrograph (print).

Several prominent features of the spectrographs can be identified easily. The atomic carbon line in the ultraviolet at 247.8 nm (2478$\mathring{A}$) appeared strongly. Three strong sets of bands

centred around 470 nm, 515 nm and 560 nm were identified as the (1, 0), (0, 0) and (0, 1) bands respectively of the C_2 Swan system ($A^3\pi_g \rightarrow X^3\pi_u$). The fainter band towards the red appeared to be the (0, 2) band of the same vibrational system. It can be seen clearly on the exposure taken with the largest hydrogen flow that there is a series of lines expanding toward the red, with one prominent line between the (1, 0) and 0, 0) bands of the Swan system. These lines were identified as the Balmer lines of the hydrogen atom. From the red end in a position almost off the photo-sensitive region of the film emulsion, the H_α line of the Balmer series can be seen at 656.2 nm. The prominent line between the Swan bands was identified as H_β at 486.1 nm, the line between two other features looking like piled-up bands as $H\gamma$ at 434.0 nm, and the remaining two lines as H_δ and H_ϵ at 410.1 and 397.0 nm respectively. The bands just to the red side of $H\gamma$ may be another member of the Swan system, the (2,0)bands at 438.2 nm, and that to the u.v. side of H_γ may be the CH 431.4 nm system, but more detailed identification is needed.

A continuous emission can also be seen in the arc spectrum, which covers about the same spectral range as the carbon arc continuous emission for the same exposure density. When comparing the spectra for different total hydrogen flows, it can be noticed that the atomic hydrogen radiation occurs over a narrower part of the arc for the greatest total hydrogen flow. It is reasonable to expect that of the total hydrogen flow, only the hydrogen flowing up past the anode would influence the radiation from hydrogen atoms just above the anode. The narrow width of atomic hydrogen

radiation then corresponds with 28 g h^{-1} of hydrogen from an annular jet of hydrogen with a velocity of 6 m s^{-1} (at room temperature) at its point of entry around the anode only 10 mm from the anode tip. The broad radiation width corresponds with hydrogen flows of 9 and 6.5 g h^{-1} issuing in a jet along the anode, with velocities of 2 and 1.3 m s^{-1} at the same point of entry. It appears that the Balmer radiation was from the centre of the arc which normally is itself concentric with the anode. These observations suggest a significant cooling of the arc by the hydrogen jet, to the extent that hydrogen atoms with a principal quantum number of three were scarce. This in turn means that the hydrogen atoms which were outside the radiating core of the arc were either not raised to the radiating state, or were very sparce. It is significant that the C_2 band radiation was of approximately the same intensity right across the arc, indicating perhaps the slower relaxation of the vibrational mode with the cold hydrogen flow. If the hydrogen atom electron temperature was in equilibrium with the C_2 vibrational temperature on the other hand, and these temperatures were in equilibrium with the collisional temperature, the narrowing of the Balmer radiation region would merely show a drop in the temperature in the outer layers of the arc. The fact that the intensity of the continuum, like the C_2 radiation, remained approximately constant across the arc, although presumably originating from another species, supports the latter view.

When one compares the arc exposures on the same spectrograph print taken with the same exposure time 0.1 s and

FIGURE 6.7 SPECTRAL MICRODENSITOMETER TRACE

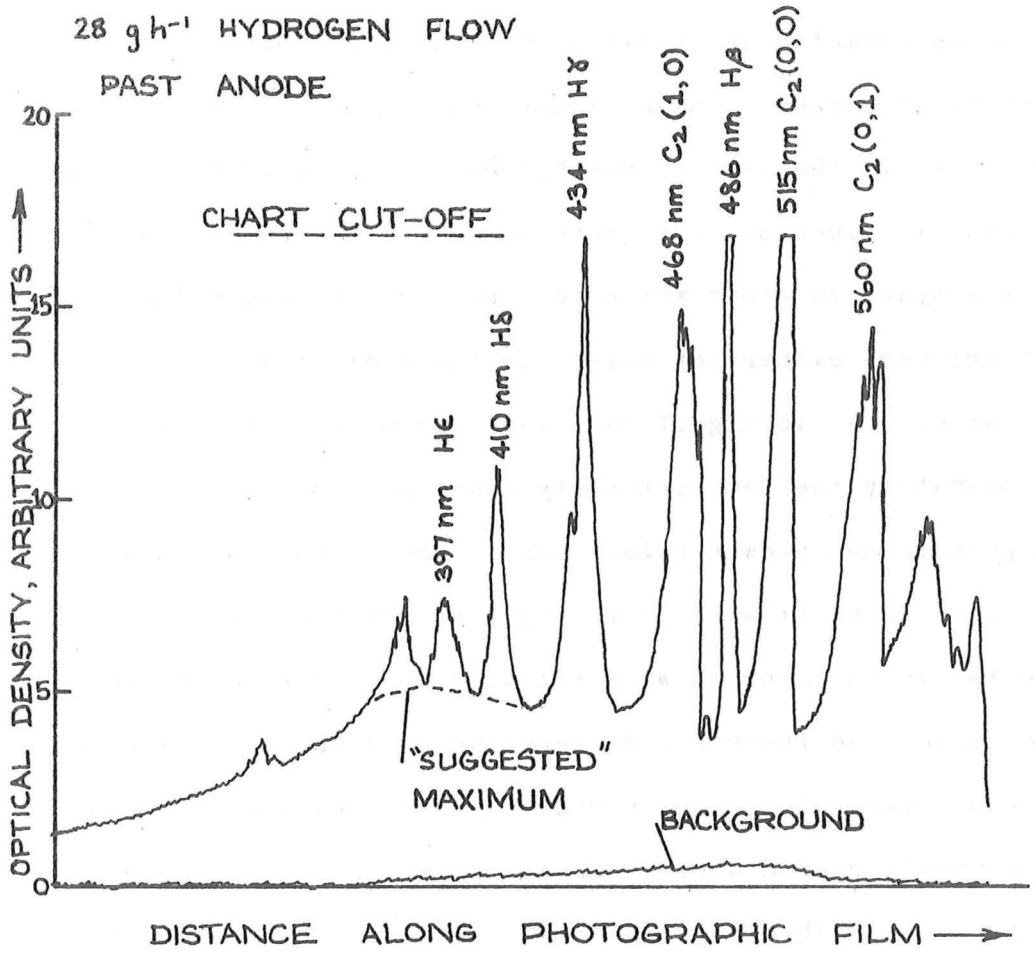
0·1 s EXPOSURE

SPECTROGRAPH EXPOSED WITH LIGHT FROM A 17A ARC, ABOUT 1MM IN FRONT OF 3·3MM D ANODE

TRACE MADE DOWN CENTRE OF BALMER LINE RADIATION ON SPECTROGRAPH

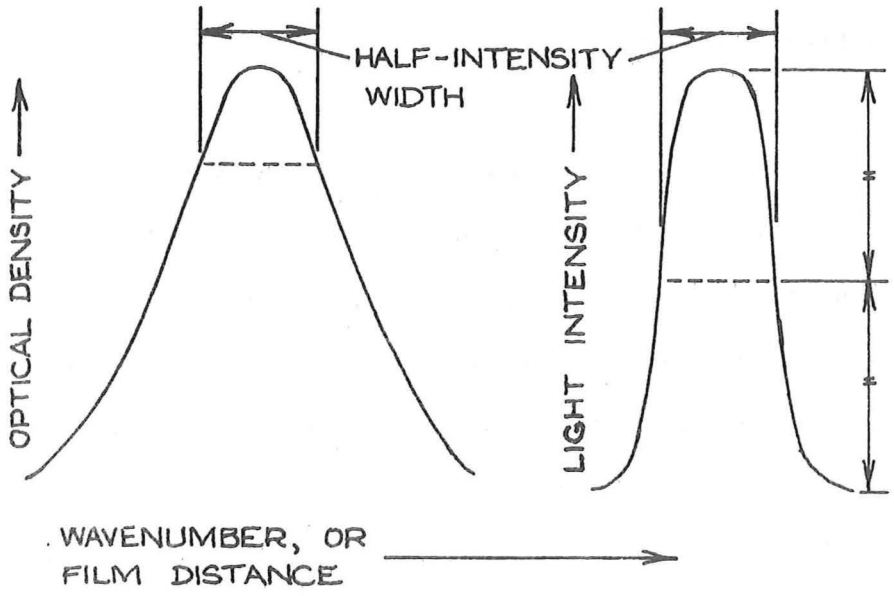
5·5 g h^{-1} CARBON ABLATION RATE

28 g h^{-1} HYDROGEN FLOW PAST ANODE

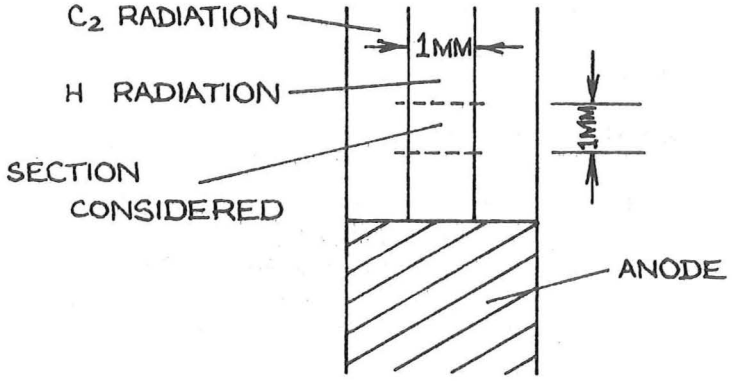


with the highest hydrogen flow 28 g h^{-1}, but with different arc currents, one notices that for the higher current the continuous emission was much stronger. The Balmer intensities were, in contrast, about the same. The lower current of 17 to 18 A corresponded to an ablation rate of 5.5 g h^{-1} whereas the higher current of 24 A corresponded to an ablation rate of 13 g h^{-1}, so it is reasonable to associate this increase in continuum intensity with an increase in carbon ablation.

Some quantitative measure of intensities was possible with the use of a Joyce null-reading microdensitometer. Figure 6.7 shows a typical trace from the microdensitometer chart recorder. It is that from the centre of the hydrogen radiation for the 17 A arc. A similar trace was made of each of the calibration exposures, and suitable wavelength positions between the molecular radiation were chosen to construct a calibration of the film emulsion. Radiation from wavelengths 365, 395, 430, 480 and 525 nm was used, and the photographic "density" (D) was measured as the ordinate of the microdensitometer trace at these wavelengths. The intensity of radiation (I) from the carbon anode of the reference arc at these wavelengths was known (2), as was also the exposure time, t. A calibration was then made of D as a function of ln (It) for each wavelength above. In effect, only 5 points were available for each calibration, as a comparison was needed between the exposures with the diaphragm inserted and those without, to determine an effective time scale for the former. These calibration curves changed gradually with the wavelength, and some interpolation was necessary to apply them



ANALYSIS OF Hβ BALMER LINE



ARC MODEL

FIGURE 6·8

to the arc features. To obtain the intensity, I_l, of a line, the density D_b, of the background around the base of the line was noted from the chart, as also was the density of the peak, D_p. From the calibration, the product It for both the peak and base was obtained. Since the exposure time t was known, the intensity of the line $I_l = I_p - I_b$, was found.

Some idea of temperatures can be obtained by considering (within an order of magnitude) the absolute intensities of radiation from the Balmer lines. The H_β line in the centre of the 17 A, 28 g h^{-1} hydrogen flow exposure had an absolute radiance of about 20 x 10^4 W cm^{-2} sr^{-1} cm^{-1} wavenumber, and since the half-intensity width of the line was 2.4 nm, the radiant intensity from the side view of the arc was 20 x 10^4 W $cm^{-3}sr^{-1}$ x 2.4 x 10^{-7}cm = 4.8 x 10^{-2}W $cm^{-2}sr^{-1}$. Considering a 1 mm section of the arc core, that is a cube of side 1 mm (see figure 6.8) and the total radiation from each side to be π times the intensity, then 6π x 4.8 x 10^{-4}W is radiated from 1 mm^3, i.e. a radiation of 9 x 10^3W m^{-3}. According to Robinson and Lenn (3), who present the volumetric radiation from the H_β line as a function of temperature and pressure, this value corresponds to a temperature of 7 or 8000K for a total pressure of hydrogen atoms of 1 bar, but about 10 000K for a total pressure of hydrogen atoms of 0.01 bar.

The radiation from C_2 was about the same magnitude as the Balmer series radiation. At thermodynamic equilibrium for a pressure of 1 bar in a carbon rich system, the mole fraction of C_2 reaches a maximum of the order of 10^{-1} at about 5000K, but

drops off for higher temperatures, becoming about 10^{-4} at 10 000K. Of those C_2 molecules which exist, only those in the upper electronic state can radiate, but only a fraction given by the transition probability (0.01 (4)) will on average radiate. It appears from this that the temperature of the gas region in the arc from which C_2 radiation was emitted may have been less than 10 000K. If the molecule C_3 was present in significant quantities, the analysis of Main and Bauer (5) indicates that it would be a significant radiator. The fact that the C_3 "Comet-head" group at 405 nm was not observed, even faintly, thus indicates that C_3 molecules were not present. If the carbon-hydrogen gas in the arc was near to a thermodynamic equilibrium, a calculation of compositions by the author shows that the C_3 mole fraction has a maximum of about 5×10^{-2} at 4500K and drops sharply with increasing temperature, to about 10^{-4} at 6000K. Thus once again under the equilibrium assumption, we have a limit on the temperature in the arc, this time a lower limit of about 6000K.

A more serious attempt to measure temperatures of the arc was made by using the relative intensities of the Balmer series, and the relative intensities of the Swan system. The intensity of any emission spectral line I_{mn}, can be related to the number of molecules of that particular species in the upper state N_m, by

$$I_{mn} = A_{mn}(E_m - E_n)N_m$$

$$= A_{mn}h_{mn}N_m$$

where I_{mn} = intensity of transition from state m to state n,

A_{mn} transition probability between the same states, s^{-1},

and E_m, E_n = energies of the respective states.

Further, if one assumes thermal equilibrium within all the molecules of that species, N_{mn} can be related to the total number of that species, N, and the temperature by

$$N_m = N \frac{g_m e^{-E_m/kT}}{Q}$$

where g_m = degeneracy or "weighting" of the state m,

k = Boltzmann's constant,

and Q = partition function for the molecule (a sum of terms similar to that in the numerator for other energy states of similar type to state m),

Thus $I_{mn} = [A_{mn} h \nu_{mn} g_m N/Q]\exp(-E_m/kT)$.

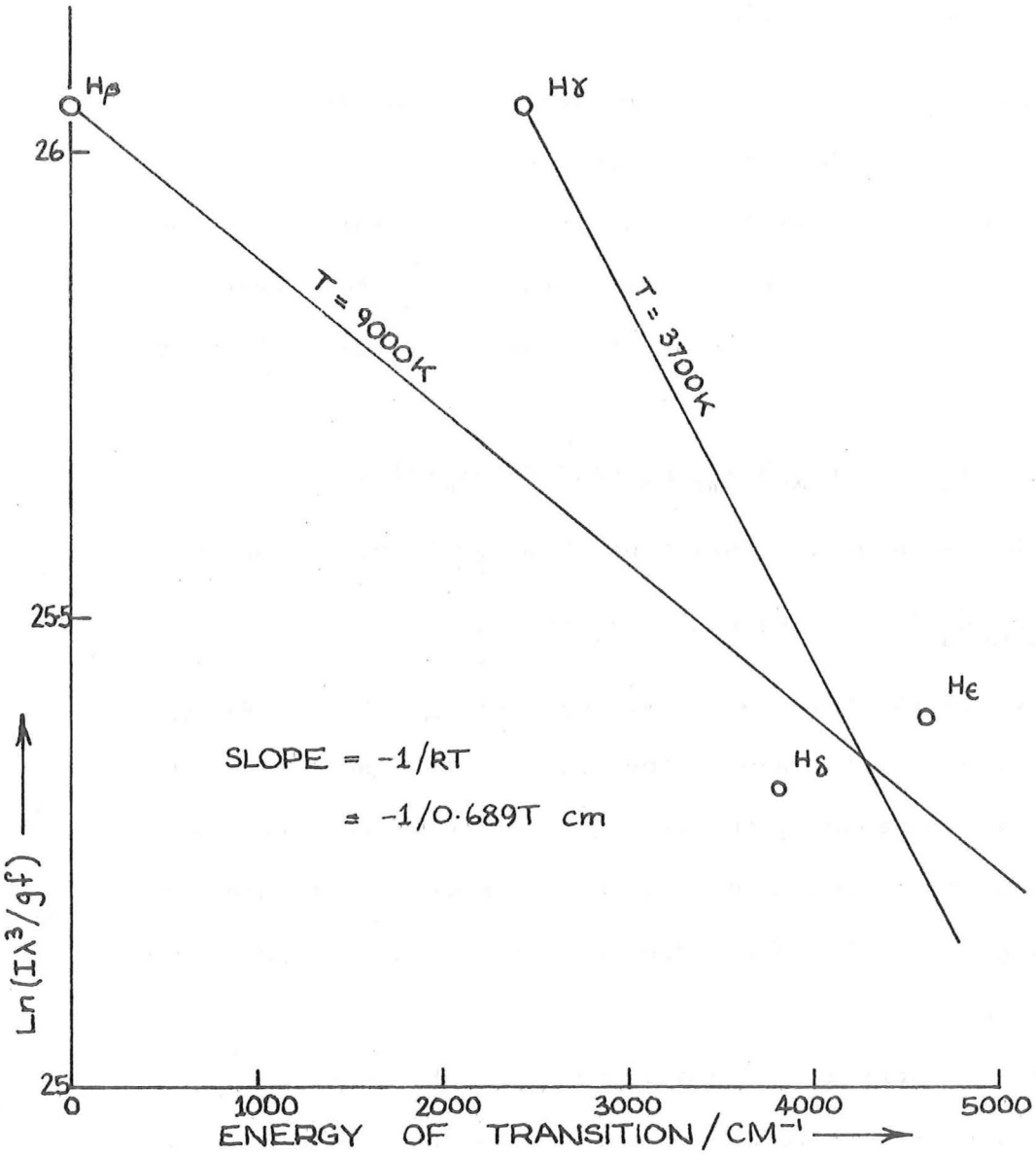
Logs may be taken of both sides of this equation, giving

$$\ln[I_{mn}/g_m A_{mn} \nu_{mn}] = (\text{constant}) - E_m/kT$$

If the term on the left is plotted against E_m for several E_m, a straight line results, whose slope is - 1/kT. Note that for a straight line to appear, thermal equilibrium is required only among the upper states used, and the parameter T obtained from this straight line is only a "temperature" of these upper states which are used.

In the application considered here, the results may be complicated by two factors. First the radiation was not radially resolved, (the Abel integral problem), and secondly with the Balmer lines, some self-absorption may have occurred. Both factors would generally cause a nonlinearity of the above plot. The transition probability if sometimes listed in terms of the

FIGURE 6.9 ELECTRONIC TEMPERATURE OF ATOMIC HYDROGEN IN THE CENTRE OF A 17 A CARBON ARC



strength factor, f, of the equivalent oscillator

$$f_{mn} = 1.5 \times 10^{-14} \lambda^2 A_{mn}$$

where λ = wavelength in nm.

The product of g_m and f_{mn} for emission is equal to the product of g_n and f_{nm} for absorption, the last being more accessible to measurement than the emission strength factor. The $g_n f_{nm}$ products were obtained for the Balmer series from Allen (6), and are listed in Appendix 2. Thus for the atomic hydrogen radiation, $\ln(I_{mn}\lambda^3_{mn}/g_m f_{mn})$ was plotted against E_m. Figure 6.9 shows such a plot for the spectrograph shown previously with a hydrogen flow past the anode of 28 g h^{-1}. The slope of a line drawn through the points is so much in doubt that even the range of temperatures indicated, 3700 to 9000K, may be meaningless.

Johnson (7), in a project related to this work, made two estimations of the electronic temperature of hydrogen atoms in a carbon-hydrogen arc. Using the same technique and spectrograph, he studied the radiation from an arc struck between two vertical graphite electrodes in hydrogen. An attempt was made to enlarge the diameter of the arc by rotating the container wall. An arc of about 20 mm diameter was formed for arc gaps of about 10 mm and currents of 8 and 22 A. From a spectrograph of the radiation from the axis of the arc, he obtained plots analogous to figure 6.8, but with much better linearity. Johnson obtained 5150K and 5350K for the electronic temperature of hydrogen for arcs of 8 A and 22 A respectively.

A similar attempt was made with the C_2 Swan system in this

reactor, to measure the vibrational temperature. The transition probability data was available in convenient form in Bleekrode's work on the spectra from a flame (8). Only one plot was made, which showed that the ordinates for the three vibrational bands (1,0), (0, 0), and (0, 1) were out of line to a large extent, with the individual "lines" of each band not following any consistent pattern.

On the other hand, Johnson obtained plots for the C_2 Swan system which were much closer to a single line, and calculated vibrational temperatures of 8900 and 7800K for 8 A and 22 A arcs respectively. It is suggested that the lack of linearity of the plots for both hydrogen and carbon with the reactor of this study could be caused by the much sharper temperature and radiation gradients in the reactor, than found in Johnson's device. An Abel integral analysis would be more important with the small arc, to determine the radial distribution of radiation from the lateral distribution, which was the distribution used here. Another cause may have been the increased absorption from C_2 and H in the cooler regions, with the reactor, although no line inversions were observed. Still another reason may have been the relative slowness of vibrational and electronic relaxation compared to the residence time in the reactor.

The exposure shown in Plate 6.1 for a current of 24 A showed a continuous emission density in the red end of the spectrum which was similar in profile to that of the carbon arc standard, and about 1/10th its absolute intensity. Hattenburg showed that his graphite arc radiated essentially as a blackbody of temperature 3792K from

580 to 800 nm. The film spectrographs made in this work show an optical density maximum at about 640 nm for the carbon arc, which is accounted for by a rapid fall-off of the film response towards 700 nm. The intensity of a 3792K blackbody per unit wavenumber (per unit length on the film) has a maximum (according to $\lambda_{max}T = 0.5099$) at $\lambda_{max} = 1340$ nm, so that at 700 nm the intensity is still rising slowly for such a body. The fact that the optical density of the arc continuum and the carbon blackbody appear to have similar contours cannot then be used to estimate accurately the effective blackbody temperature of the arc radiation, but an upper limit can be placed on the temperature. It is not expected that the maximum of the arc radiation has a wavelength as small as 700 nm, placing an upper limit of 7500K on the effective blackbody temperature. The maximum in optical density at a wavelength of about 380 nm in figure 6.6 is deceptive, and corresponds to a low intensity of background light almost constant from 350 to 500 nm, after the film sensitivity is allowed for.

Thermopile Readings

A compensated "Moll" thermopile made by Kipp and Zonen was used to measure the total radiation incident on the projection screen from the anode and from the arc. The thermopile used a fluorite window with transmission from a wavelength of 140 nm in the ultraviolet to one of 10 μm in the far infrared.
A calibration for the instrument was not available, but nominal values given by the manufacturer indicate a thermocouple e.m.f.

of 12 μV per W m^{-2} received in the plane of the thermopile, for the largest diaphragm. For a rough estimate of absolute values of radiation, the limiting solid angle of the light path through the window and lens was determined. This proved to be the solid angle subtended by the far end of the quartz window from a point near or on the anode, and had the value 6×10^{-4} sr. All light rays in this solid angle from a point in the centre of the reactor contributed to the intensity of the focussed point on the screen, whereas all light rays outside this solid angle were scattered or absorbed. Since the quartz window transmitted only over the wavelength range 170 nm to about 3.3 μm, and the old quartz lens probably transmitted from 220 nm to about 3 μm, the latter was the limiting spectral range.

Two readings were taken with the thermopile aperture as far forward on the tip image of the anode as was possible. Both readings were taken with a current of 16 to 17 A, during the run in which the colour photographs shown in the frontispiece were taken. The aperture had a diameter of 8 mm, and covered a large part of the anode image, which was 11 mm across. A steady reading of 0.9 to 1.0 mV was obtained, but in another attempt a fluctuating reading was obtained, with a rough mean of 0.7 mV. Taking the 1.0 mV reading, this represented an energy flux of $1.0 \times 10^3/12 = 80$ W m^{-2} through the plane of the thermopile. Allowing for the magnification factor of 3.3 through the lens, this corresponded to an intensity of $80 \times (3.3)^2 = 900$ W m^{-2} from the anode through a solid angle of 6×10^{-4} sr. Thus the normal intensity per unit solid angle = $900/6 \times 10^{-4} = 1.5 \times 10^6$ W $m^{-2}sr^{-1}$, and the total

hemispherical radiation from the anode surface = $\pi \times 1.5 \times 10^6 = 5 \times 10^6 W\ m^{-2}$. If this came from a 3800K blackbody, radiating $12 \times 10^6 W\ m^{-2}$, over 90% of the radiation would be included in wavelengths less than 3 m, i.e. $12 \times 0.9 = 11 \times 10^6 W\ m^{-2}$ would be observed. Radiation from a 3200K blackbody amounts to $6 \times 10^6 W\ m^{-2}$, and about 85% would pass in wavelengths less than 3 m, giving $0.85 \times 6 \times 10^6 = 5 \times 10^6 W\ m^{-2}$ observed. Thus the average temperature observed on the anode surface from the side was about 3200K for the 17 A arc.

Two thermopile readings were taken of the arc itself, in positions just in front of the anode, with currents from 45 to 50 A. The readings are presented below, together with the carbon ablation rates recorded at the time, and the hydrogen flow past the anode.

Carbon rate/g h^{-1}	Anode hydrogen/g h^{-1}	Thermopile reading/mV
45	14.5	0.21
55	22.5	0.4

According to the analysis presented above, the 0.4 mV signal corresponded to $0.4 \times 5 \times 10^6 = 2 \times 10^6 W\ m^{-2}$, or $2/11 \simeq 0.2$ of the radiation from a 3800K blackbody placed centrally in the reactor. Similarly the 0.21 mV reading corresponds to 0.1 of this radiation. As discussed before, these isolated carbon rate readings were not reliable, but no applicable current readings were available for better estimates.

Photographs

From the coloured photographs presented in the frontispiece, it can be seen that a blue colour appeared in the vicinity of the

arc, often with a red-purple streak in the centre of the blue for low current arcs. For larger currents than about 30A, the red colour appeared only around the cathodes, and moved about vigorously. Also with larger currents, a milky haze appeared in the arc chamber.

From the spectrographs, the C_2 Swan band radiation ((1,0) 470 nm) predominated in the blue visible wavelengths (425-490 nm) with some H_β radiation from the atomic hydrogen Balmer series contributing (486 nm). The red colour in the photographs corresponded to a wavelength from 600 to 700 nm. Two possibilities were considered; tungsten and hydrogen. The atomic lines of the tungsten atom observed in arcs are listed (9) as having wavelengths of 400.8, 429.4 and 430.2 nm, whereas the lines from singly ionized tungsten have even shorter wavelengths. The radiation was thus not likely to be from tungsten in the gas phase, nor from tungsten in droplet form, as the continuous emission from the drops would have had a white colour at the temperature the drops would assume. The H_α line of the Balmer series with a wavelength of 656.2 nm was, on the other hand, a very likely answer, for the colour agreed, and the position of the red region corresponded with the position of the Balmer radiation for low current arcs.

All the photographs shown were taken with the same shutter setting and exposure time (f 2.8, 1/60 s), were developed and printed at the same time using the same procedure, so that some comparison can be made between the photographs regarding radiation intensities. With the higher current, it can be seen that the anode tip radiated at a higher temperature from the side.

Comparing the end-on view of the cathode before carbon build-up with the side view of the anode in the low current run, the tungsten tips appeared to operate at temperatures below 3200K. The origin of the white spot in the centre of the tunsten tip was not obvious. It may have been caused by radiation from a hotter region of the tungsten surface at the arc spot, may have been from the initial patch of carbon deposit, or may have been an apparent concentration of the continuous emission in the arc stream from the cathode, which was viewed end-on. It is seen that as the cathodes were built up with deposit, they became brighter, almost to the brightness of the anode.

When one looks at the space between the cathode and anode in the first low current photograph, it is seen that the walls around the electrodes were relatively cold.

6.4 Carbon Measurements

Several measurements were made of the mass of carbon which appeared in various forms after a run. Only 3 or 4% of the carbon fed to the reactor was found as soot. About 1% was sometimes found in leaf form. For the runs investigated, by far the largest part of the solid carbon found was found deposited on the graphite exit tube or on the cathodes. Of four runs with currents from 30 to 35A, from 12 to 27% of the carbon fed was deposited on the inside of the exit tube, as determined by a weight increase. On the other hand, operation at a small current with a split-tip cathode resulted in a slight decrease in exit tube weight. Only a slight dusting of soot was observed

on the chamber floor after any run, and a slight erosion was seen of the chamber wall below the cathodes. Some electronmicrographs were made of the soot lifted off the wall in two places. Plate 6.2 shows an electronmicrograph of soot taken from the front face of the probe in the cooler, which faced upstream into the flow from the quench tube. The run which produced this soot was characterised by:-

10A for 10 minutes, total H_2 28 g h^{-1} followed by
20A for several minutes, total H_2 36 g h^{-1},
graphite cathodes,
small graphite exit tube,
and quench tube not insulated from earth.

It is seen that chains of uniform, smooth 'balls' of diameter 85 nm make up the soot. This is consistent with the description of soot obtained from flames, but has balls of larger diameter than those commonly found in flames (10 to 50 nm).

Plate 6.3 shows an electronmicrograph of soot taken from the inside wall of the water-cooled brass end-plate with no exit tube in place. The run was characterised by:

10A for 20 minutes, total H_2 18 g h^{-1} followed by
20A for 3 minutes "
graphite cathodes,
and no exit tube.

The sample was taken from an area exposed to the arc, and shows much less defined chains, or aggregates, of particles from 40 to 50 nm in diameter. The edges and the optical density of the particles are irregular, compared with those of the previous

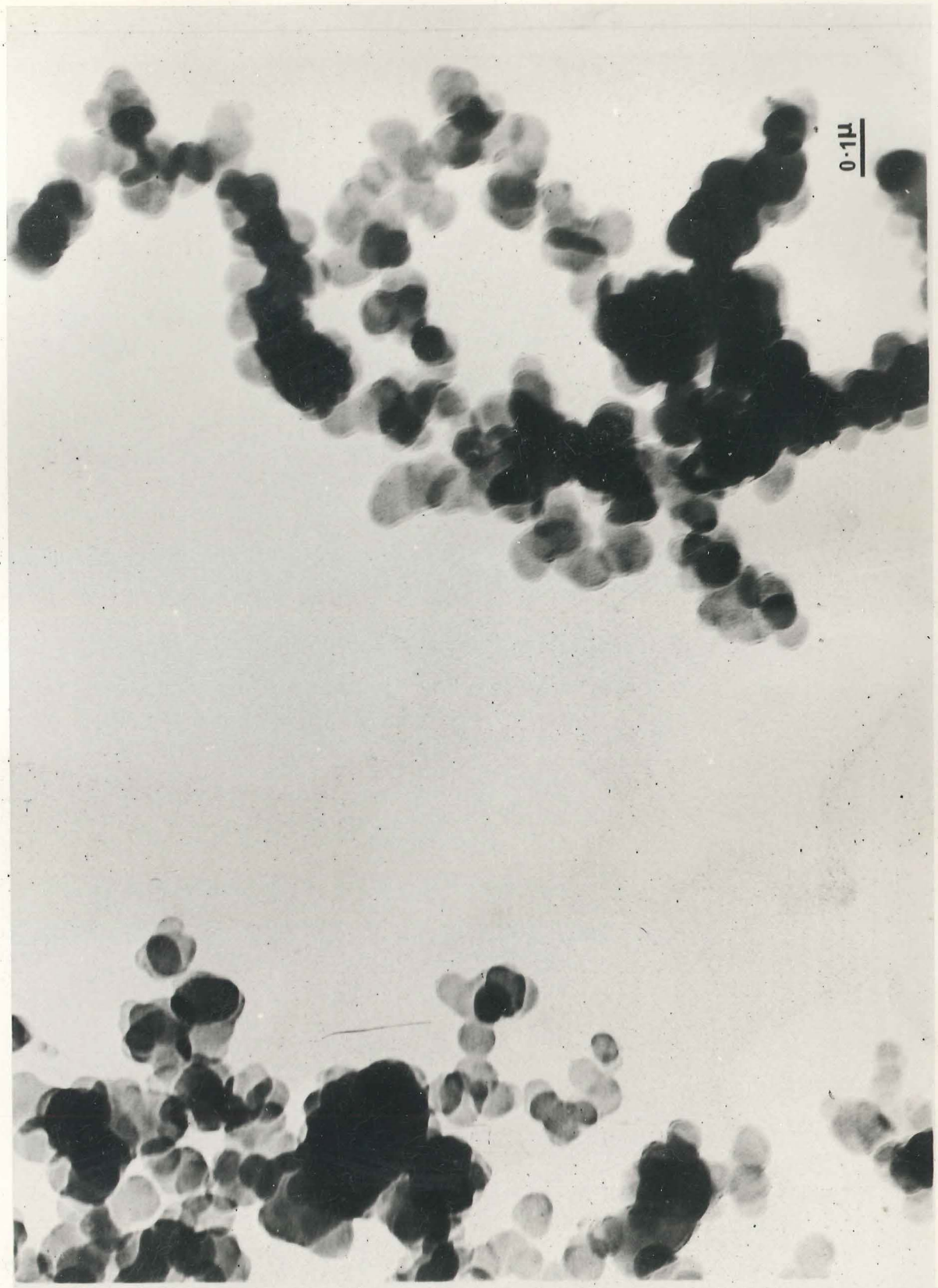


PLATE 6·2 ELECTRONMICROGRAPH OF SOOT COLLECTED DOWNSTREAM OF THE QUENCH TUBE

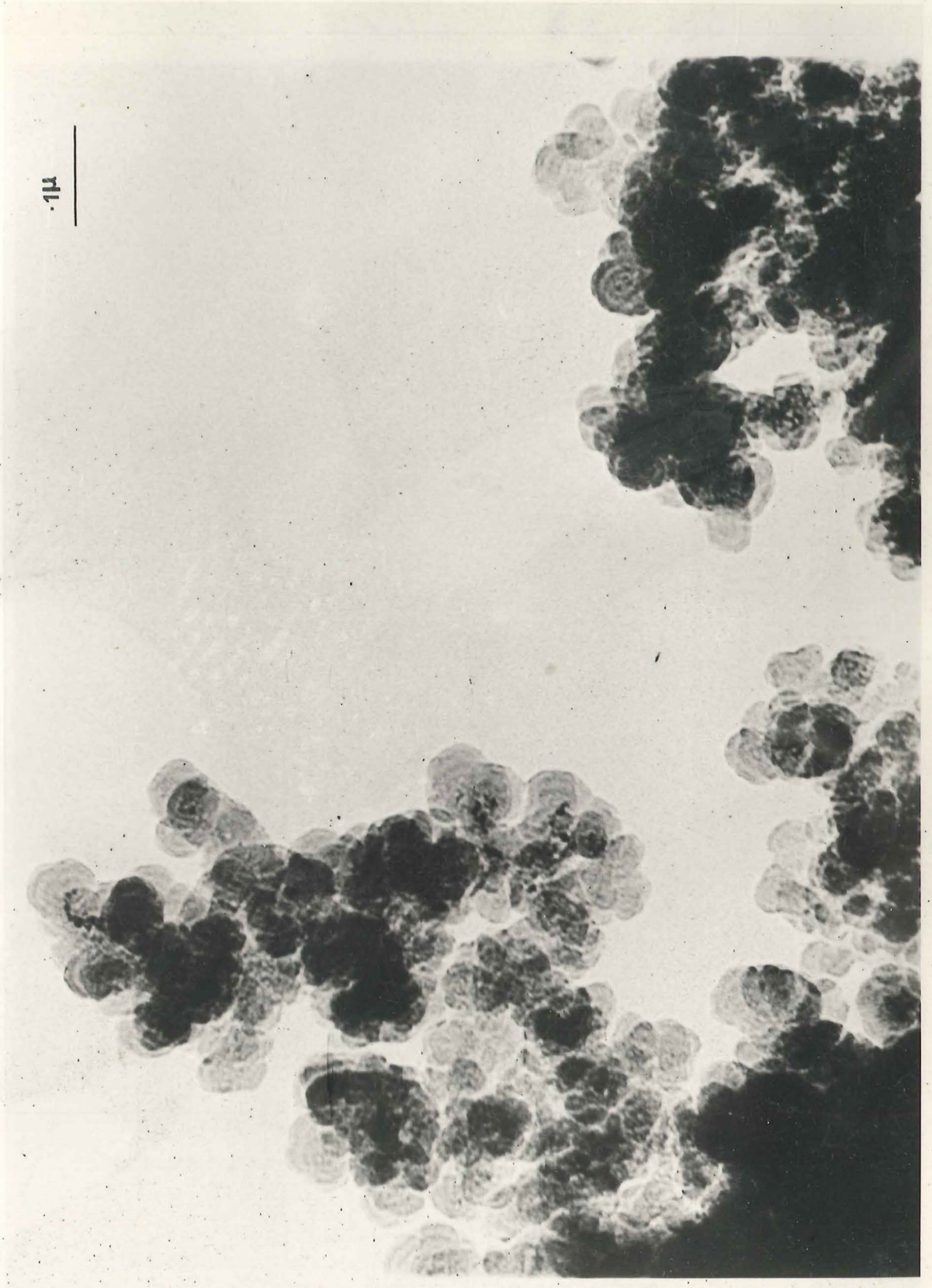


PLATE 6·3 ELECTRONMICROGRAPH OF SOOT TAKEN BEFORE REACHING THE QUENCH TUBE

electronmicrograph. It is interesting that the irregular contours of the edges of the particles are repeated by smaller patterns toward the centre of each, suggesting that these particles were in a state of growth when they deposited.

Experimental Accuracy

Under this heading will be discussed errors of measurement, and experimental inconsistencies.

Carbon mass flow

The calibration of the velocity of the carbon rod with triac setting showed a total scatter of 10% for the lowest velocities, and 3% for the highest velocities used. Since errors of this magnitude were expected from the time and distance measurements for the velocity, a smaller actual variation in velocity was indicated for any given setting of the triac. The determination of the mass of carbon per unit length of rod (13.0 g m^{-1}) was reproducible to $\pm$4%. Under run conditions when time was short, the triac could be read to the nearest division only, corresponding to an uncertainty of $\pm$ 10% for the carbon flow at low settings, and to $\pm$1% at high settings. Thus total uncertainty in the mass flow may be estimated as $\pm$7% at the higher flows.

Hydrogen mass flow

A calibration of the Fischer and Porter "flowrator" bob position against the volumetic flow of hydrogen through it showed a scatter of $\pm$3% when the pressure at which the volume of gas was measured, and the pressure of the "flowrator" were

both atmospheric. The mass of gas was estimated from the measured atmospheric pressure. Owing to restrictions in the gas flow system of the reactor, the pressure in this hydrogen feed flowrator rose to about 0.06 bar above atmospheric for the higher flows. A calibration was thus also made for a flowrator pressure of 1.06 bar, which showed a rise in flow compared to a pressure of 1 bar for the same flowrator reading, of about 8%. Interpolations were made between these two calibrations (1.00 bar and 1.06 bar) when using them. A probable error in hydrogen flow rate was ±5%.

Mass balance

With the assumptions that no hydrogen was lost from the mass flow through the reactor, and that the product consisted only of hydrogen and acetylene, two checks on the mass flows were possible. By using the readings from the product gas rotameter, which was calibrated for both 100% acetylene and 100% hydrogen so that interpolation could be used for intermediate compositions, some rough idea of the mass flow in the gas from the reactor was obtained. This was then compared with the fraction of the measured ingoing mass streams calculated to be in the gas phase. The two calculated values differed by up to 50%, and down to 10%, but always with more measured in the product stream than calculated. Unfortunately the product rotameter was used over the lower part of its range where the likely uncertainty was ±15% of the total flow. The second check on mass flows was confined to the carbon flow. Of the measured carbon inflow, a certain fraction was calculated to be present in acetylene according to the gas analysis. The remainder was expected to be found as soot or deposited carbon.

Several checks of this kind made for 30-35A runs with only lightly coated cathodes accounted for 88, 61, 63 and 81 % of the carbon fed. The soot formed was accurately measured, but the carbon deposit about the walls was measured only for the walls of the exit tube. The largest discrepancy was about 1.6g of carbon, or that in a cube of 9 mm side. It was difficult to account for this additional mass of carbon required to make a balance.

Energy flows

The wattmeter which was used to measure the electrical power fed to the reactor was checked against voltage and current readings taken at the same time as those of the wattmeter. Replacing the reactor by a suitable resistive load so that the power dissipated was steady, the product of current and voltage agreed with the wattmeter reading to within 6%, the accuracy to which the current could be read. The water flows through each section of the apparatus (62 g s^{-1} through quench, 27.5 g s^{-1} for reactor and cooler) could be set to within 1% of the calibrated values. Calibrations made for the thermocouple-water flow combination against the wattmeter were within 3% of each other. These calibrations were checked after 6 months use, and 4% correction was necessary for the reactor system, 10% for the quench system and 4% for the cooler system.

After these calibrations, it was surprising to find an unexplained loss of energy from the reactor of from 12 to 30% of the input energy. This was traced to a conduction heat transfer to the heavy electrical cable connected to the anode. When this was replaced by a smaller cable for 0.1 m from the

anode, the measured energy output to the cooling water agreed to ±4% with the electrical energy input.

Acetylene analyses

All the acetylene concentrations quoted as being "reliable" were made with a gas sample of about 4.9 cm^3 colume. For a sample with 10 mol % concentration of acetylene, about 3.7 cm^3 of 0.011 Normal sodium hydroxide solution was used as a titre. A colour change for the titration could be detected over two drops of the solution, corresponding to about 0.04 cm^3, or 1% error in an acetylene concentration of 10 mol %, and 10% error in a concentration of 1 mol %. The volume of the sample was closely reproducible from the mechanical action of the sampler, but the pressure at which the sample was taken could change. The sampling pressure was controlled to within 2 mm of mercury of atmospheric pressure, but no record was kept of the latter, which could have changed by ±5%. Thus the expected error in acetylene analyses ranged from ±6% for the larger concentrations to ±15% for the smallest concentrations.

References Chapter 6

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TOWARDS A REACTOR MODEL

CHAPTER 7

Contents

Models for acetylene formation - experimental and thermodynamic quantities. theories for acetylene formation. testing the theories.
Particulate carbon - experimental observations. theory.
Use of above theories for model of reactor - arcs. cathode jets. cathode carboning. carbon particles and acetylene formation. anode ablation. tungsten behaviour.

Hypotheses are proposed in this chapter to explain different aspects of the observed reactor behaviour, and are compared with existing hypotheses. A description is attempted first which ignores the arc mechanism and averages over all elements of the mass flow through the reactor. The details of the arc are then discussed.

7-A Models for Acetylene Formation

A1 Relevant experimental and thermodynamic data

From the measurements of cooling water temperature rise discussed in the last chapter, estimates were made of the enthalpy of the mass leaving the reactor. The attempts made to measure all energy flows in and out of the reactor resulted in energy balances to $\pm 4\%$. As shown below, two ways of calculating the above enthalpy may then be used. With respect to graphite and hydrogen at room temperature, the specific enthalpy of the exit mass flow was given by

$$h_{ex} = (\dot{e}_a - \dot{q}_r)/\dot{m},$$

from an energy balance over the reactor alone, or

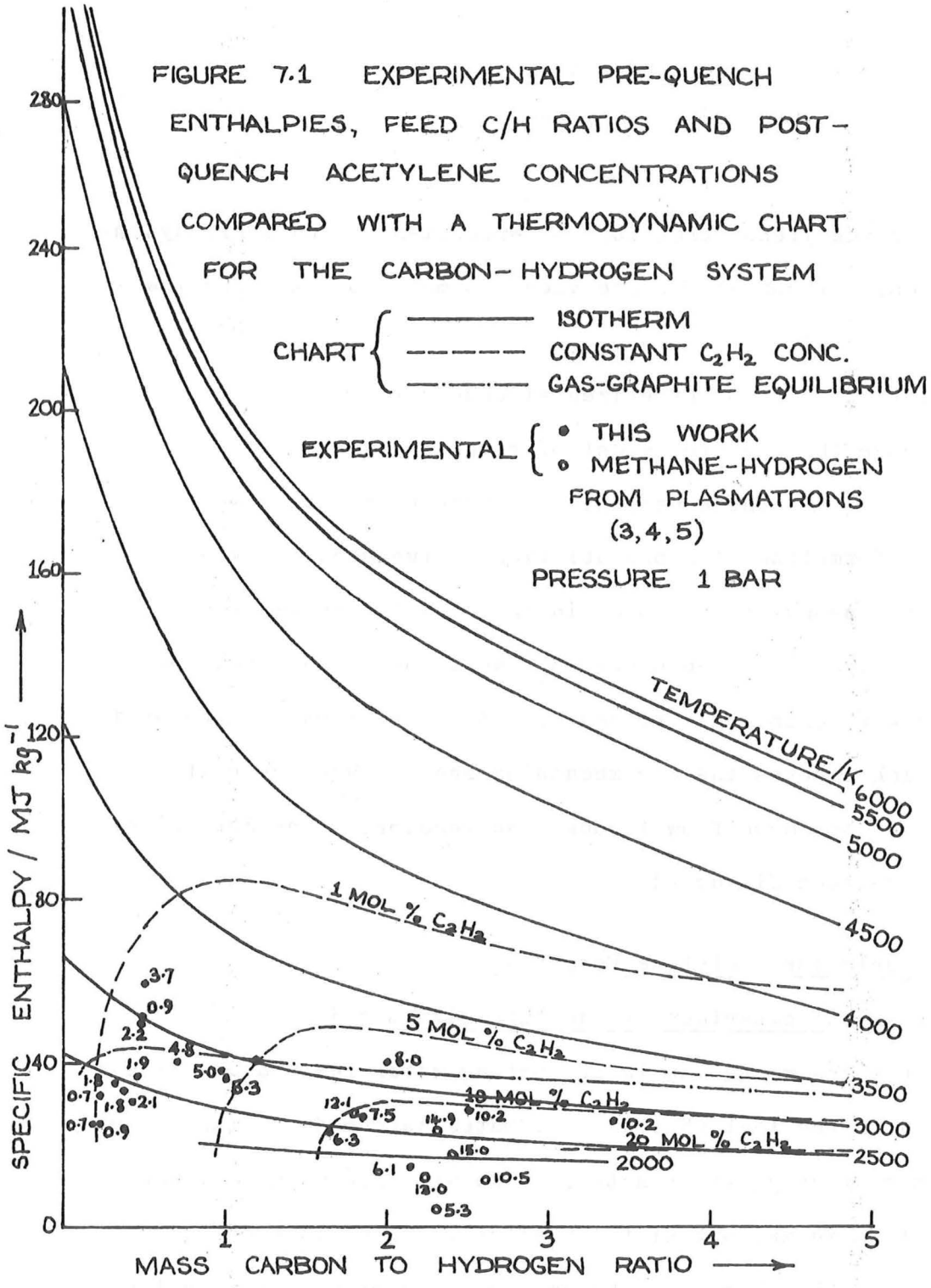


FIGURE 7.1 EXPERIMENTAL PRE-QUENCH ENTHALPIES, FEED C/H RATIOS AND POST-QUENCH ACETYLENE CONCENTRATIONS COMPARED WITH A THERMODYNAMIC CHART FOR THE CARBON-HYDROGEN SYSTEM
CHART
ISOTHERM
CONSTANT C_2H_2 CONC.
GAS-GRAPHITE EQUILIBRIUM
EXPERIMENTAL
THIS WORK
METHANE-HYDROGEN FROM PLASMATRONS (3,4,5)
PRESSURE 1 BAR
TEMPERATURE/K
6000
5500
5000
4500
4000
3500
3000
2500
2000
1 MOL % C_2H_2
5 MOL % C_2H_2
10 MOL % C_2H_2
20 MOL % C_2H_2
SPECIFIC ENTHALPY / MJ kg^{-1}
MASS CARBON TO HYDROGEN RATIO
0
40
80
120
160
200
240
280
1
2
3
4
5

h_{ex} = $(\dot{q}_q + \dot{q}_c + \dot{e}_{ch})/\dot{m}$, from an energy balance over the quench and cooler,

h_{ex} = specific enthalpy of the mass leaving the reactor, kJ g^{-1},

$\dot{e}_a$ = rate of energy dissipation associated with arc, kW,

$\dot{q}_r$ = rate of heat transfer from reactor to cooling water, kW,

$\dot{q}_q$ = " " " " " quench " " " , kW,

$\dot{q}_c$ = " " " " " cooler " " " , kW,

$\dot{e}_{ch}$ = rate of transport of chemical energy from the cooler with the product stream, kW,

and $\dot{m}$ = rate of transport of mass from the reactor, g s^{-1}.

The temperature of the mass entering the reactor was at "room temperature", and that of the mass leaving the cooler was not above 400K, for the small steel tube leading from the cooler was cool to the touch. Experimental enthalpies were calculated with their zero at these two temperatures from the two equations respectively, and in a comparison with enthalpy data obtained elsewhere, whose zero was 298K, the difference in reference temperatures was ignored.

The first method for calculating the specific enthalpy involved the small difference of two large terms, as the heat transfer rate from the reactor was from 85 to 90% of the power input. Thus a likely error of $\pm$3% in reading the wattmeter, a $\pm$3% error in the rate of heat transfer from the reactor, and a total error of about $\pm$12% in the mass flow rate, may lead to errors in the calculated enthalpy of $(3 + 3)100/15 - 12$ $= 40 + 12 = \pm$ 50%. Accordingly the second method was used,

with an expected error of $14 + 12 \simeq \pm 25\%$ for small C/H ratios and $5 + 12 = \pm 17\%$ for the larger C/H ratios.

A computer program was written to calculate the composition of the carbon-hydrogen system for temperatures from 2500 to 6000K and for atomic compositions ranging from all hydrogen to all carbon. The free energy data of Duff and Bauer (1,2) was used, but only 23 species were considered, compared to the 71 species used by Duff and Bauer. A hand calculation was performed to determine the contribution to the total enthalpy from the various species, and the 23 species with a contribution greater than 0.2% of the total over the temperature range 2500-6000K, were chosen. These species were C, C_2, C_3, C_4, C_5, C_6, C_7, CH, C_2H, C_3H, C_4H, C_5H, C_6H, C_7H, C_9H, CH_2, C_2H_2, C_3H_2, C_4H_2, C_6H_2, CH_4, H and H_2. Calculations of compositions with these species considered, gave mole fractions corresponding to those of Duff and Bauer within the accuracy that their graphs could be read ($\pm 5\%$). The total enthalpy, entropy, Gibbs free energy, (on both mass and molar basis) and average molecular weight were also calculated for each temperature and C/H ratio. The total pressure was set at 1 atmosphere for all calculations.

Figure 7.1 shows the calculated values of specific enthalpy graphed as a function of the carbon to hydrogen mass ratio, with temperature as a parameter. For full equilibrium, solid carbon was calculated to be present at specific enthalpies less than about 40 kJ g^{-1}. A line below which solid carbon is present, is shown dashed. The thermodynamic properties of polycrystalline graphite were used to calculate the points on this line.

Below this line, in the two-phase region, the quantity of hydrocarbons in the gas phase drops sharply, as shown by Duff and Bauer, so that at 3000K the only species with mole fractions greater than 10^{-2} are H_2, H and C_2H_2. Acetylene concentrations in the presence of solid carbon were calculated by them to reach a maximum of 7 mol % at about 3300K, dropping to 1 mol % at 2500K.

The maximum acetylene concentration possible under complete thermodynamic equilibrium can be found by searching the single phase results calculated for an atomic ratio of carbon to hydrogen of one (equal to that in acetylene), above the two-phase temperature (3520K), and by searching the two-phase results for temperatures below 3520K. For the single phase, the highest acetylene concentration was 5 mol %, at the temperature 3520K, and for the two-phase region the highest concentration was 7 mol % at about 3300K, as mentioned before. As the thermodynamic properties of the important species H, H_2 and C_2H_2 are well known from absorption spectroscopy, sufficient confidence may be placed in this figure of maximum acetylene concentration (7 mol %) to say that the concentrations of acetylene obtained experimentally from this work (10.2, 11.8 mol %) are not the result of complete equilibrium, at any temperature.

In figure 7.1, the single-phase calculations have been extended to temperatures lower than those of the "solid carbon line". The constant temperature lines have been extended, ignoring the presence of solid carbon. Also on figure 7.1 three constant acetylene concentration lines of 1, 5 and 10 mol % were plotted, again using the single-phase calculations.

Experimental points representing the conditions of the mass stream as it left the reactor, just before entering the quench, are also shown in figure 7.1. The source of the figures for the enthalpy have been discussed; the C/H ratio will now be looked at more closely. The C/H ratio for each experimental point on figure 7.1 was that determined from the measured inflows of carbon and hydrogen, but was not necessarily the C/H ratio of the flow leaving the reactor. From chapter 6, it was seen that for a 35A run, up to 27% of the carbon fed into the reactor was deposited on the graphite exit tube. This would lower the C/H ratio of the rest of the mass after it had passed the exit tube to 0.73 of that measured previously. Not sufficient information was obtained regarding the deposit of carbon in the reactor for runs with other currents, but if it was assumed that the difference between the measured inflow of carbon and that appearing in acetylene was deposited in the reactor, then the C/H ratio would be reduced by a factor of 2 at lower initial C/H ratios, and by a factor of 5 at the highest ratios used.

Nevertheless, when the feed C/H ratio was used for the experimental points, with several exceptions the measured acetylene concentrations followed the calculated concentration contours within experimental accuracy (acetylene concentration: $\pm$ 6% for larger concentrations, $\pm$ 15% for smaller concentrations; C/H ratio: $\pm$ 20% for small values, $\pm$ 12% for the larger values). Three exceptions lay at smaller C/H values than those given by the calculated contours, and three lay at a higher C/H value. Results of 3.7, 4.8 and 2.4 mol % lay at significantly smaller C/H ratios.

These three happened to be the only results used which were amongst the group with apparent very high conversions (~ 85%), a group which was termed doubtful in chapter 6 because of the likelihood of higher momentary C/H ratios from fluctuating currents. The results of 6.1, 6.3 and 7.5 mol % lay at a significantly higher C/H ratios than that corresponding to the same chart values. It was found that the 6.1 mol % result, the farthest out, was the only one used from a run where the arc had attached itself to a rapidly growing lump of deposit, thus reducing the carbon flow (and the enthalpy) at the exit by a large extent.

For comparison with the results of this study, several plasmatron results were studied: - work with hydrogen used as the plasmatron gas and where some information was available on the enthalpy of the mixture before quenching. These plasmatron studies used cold methane as a feed, which was fed into a hot hydrogen stream, the enthalpy of which was known. The mixture then reacted while passing down a short tube, and was quenched at the end of this. The specific enthalpy calculated and shown on figure 7.1, was the mean specific enthalpy over the two streams as they were introduced to the reaction tube. Some energy loss to the tube would be incurred before quenching, so the values of specific enthalpy used represent an upper limit for the enthalpy of the mixture before quenching. It is seen that the two acetylene concentrations, 14.9 and 15 mol %, from the studies of Kozlov et al. (3), and Anderson and Case (4) respectively, correspond with the single-phase equilibrium values.

The 12.1 mol % value from Kozlov appears too high to fit the calculated values, lying as it does on the 10 mol % line. As a further independent check, a point was calculated from Freeman and Skrivan's work with methane and a hydrogen plasma stream (5), which indicated that for a specific enthalpy from 18 to 20 kJ g^{-1} and a C/H mass ratio from 2.4 to 2.0, an acetylene concentration from 12 to 14.5 mol % was obtained. Since the hydrogen to methane ratio was not given, values of 0.5 to 1.0 mol/mol were assumed (Kozlov 0.7, Anderson and Case 0.5). It is seen that the values are close to the others presented.

A2 Theories of acetylene formation

A theory will now be proposed to account for the correspondence of the calculated partial equilibrium concentration of acetylene with the experimental values. Two further theories which have been published will then be described, and the implications of each of the three examined.

It is proposed that at some time after an operation in which carbon and hydrogen are brought together in the gas phase at a high temperature, thermodynamic equilibrium within the gas phase alone may obtain, substantially independent of any presence of carbon, real or estimated, in the solid phase. The existence of this "metastable" or "supercooled" equilibrium will depend on the out-of-balance of the rates of chemical reactions, but its composition will depend only upon the thermodynamic state, described most easily by the carbon to hydrogen ratio, and the enthalpy. The time needed to establish the metastable equilibrium will depend on the

rates of chemical reaction from the starting materials. It will accordingly depend on the nature of the starting materials, the method of heating, the mixing of the reactants and other factors influencing the gas reactions.

A limit is expected on the time during which this supercooled equilibrium can prevail (with respect to graphite), and this will be controlled by the velocity of chemical reactions in the direction of equilibrium with soot. (The form of solid carbon which is observed in such systems is soot, and it is customary to equate the thermodynamic properties of soot and graphite.) From the above argument, if the gaseous carbon-hydrogen system is held at a temperature above a certain minimum, for a time long compared to the time for completion of the gas phase chemical reactions, but short compared to the time for soot formation, one will obtain equilibrium at that temperature for the gas phase alone. It is proposed that if the gas is cooled quickly enough, for example by passage through a cold tube, then the species other than radicles are preserved, and radicles are converted to soot and hydrogen.

Another theory, proposed by Plooster and Reed in 1959 (6) to apply to their experimental situation, considered that complete equilibrium was attained at temperatures from 2500 to

2900K, between a carbon tube and hydrogen passed through with a contact time greater than 0.1s. They suggested that the products resulting from a rapid cooling of the gas were produced by the specific reactions

$$H + H \rightarrow H_2$$

$$C_2H + H \rightarrow C_2H_2$$

$C_2H + C_2H \rightarrow C_4H_2$, with the acetylene present at the higher temperature unaltered. To relate the theory to experimental results, an assumption was needed about the relative velocities of these reactions. It was assumed that the rate constants of each reaction were the same.

This theory was modified slightly by Baddour and Iwasyk in 1962 (7), and applied to the situation occurring in their graphite-hydrogen arc reactor. They proposed that complete heterogeneous equilibrium occurred downstream from their carbon arc, which operated within a graphite cylinder. When this equilibrium mixture was rapidly cooled, they proposed that only the reactions

$$2H \rightarrow H_2,$$

$$C_2H + H \rightarrow C_2H_2,$$

$$C_3 \rightarrow 3C_{(s)},$$

$$C_2 \rightarrow 2C_{(s)},$$

and $C \rightarrow C_{(s)}$ occurred, with the acetylene present at the higher temperature preserved. The assumption about reaction rates needed by Plooster and Reed was then not required in the above equations, for it was assumed (implicit in above) that <u>all</u> the C_2H species reacted with hydrogen atoms to form acetylene during rapid cooling.

A third theory, put forward by Anderson and Case in 1962 (4), applied to the reaction between cold methane and hot hydrogen from a plasmatron. Their hypothesis was that complete mixing of the hydrogen and methane occurred rapidly, and the chemical reactions

$2CH_4 \rightarrow C_2H_2 + 3H_2$, and

$C_2H_2 \rightarrow$ decomposition products, then began. The nature of "decomposition products" was stated to be solid carbon. Diacetylene and ethylene were stated to be minor products of reaction of acetylene. In their view, the composition of the gases at any time after mixing, is controlled by the rates of the two reactions given above. These rates are in turn a function of temperature and reactant concentrations, determined by a series of mass and energy balances at successive reaction times, allowing for the enthalpy change on reaction. All elements of the flow were assumed by Anderson and Case to behave in a similar fashion. Rapid cooling, as in a water spray, was assumed to preserve the composition of the hydrocarbon mixture down to room temperature, where it was observed.

A3 Testing the theories

The three theories will be discussed separately, beginning with the most particular, and ending with the most general. The argument will be related to Duff and Bauer's 1961 equilibrium compositions, which will be assumed correct. There are still some doubts about the free energy function of C_3, and improved values have appeared since 1961. However most

uncertainty attaches to the C_nH group of radicles, of which only C_2H has been identified in spectra. As will be seen, useful conclusions may be made if the above assumption is made, conclusions which lend support to the assumption. The kinetic analysis of Anderson and Case (4), and some of its predictions, have been described in chapter 2. Using a first order description of the methane reaction and a second order description of acetylene decomposition obtained below 1700K, they predict that for their conditions, acetylene formation from methane is substantially complete after 10^{-4}s, after which the temperature has dropped to between 1700 and 2000K. Both reactions considered are relatively slow and almost balanced at these temperatures, so that it is not until several milliseconds have passed that appreciable acetylene is lost. The acetylene concentration at the "plateau" from such an analysis is not related to equilibrium values, for the reverse reactions are not considered. Rather, they depend on a balance of the two irreversible reactions considered, and mass and energy conservation.

One of the conclusions of the theory of Anderson and Case is that the supply of energy to the mixture in excess of what would be required to raise it to about 1800K will allow acetylene to form faster than it decomposes. At a given hydrogen to methane ratio, the methane conversion to acetylene is predicted to be a function of the enthalpy of the starting mixture, independent of reaction time (within certain limits) and independent of whether the energy was introduced with the methane or with the hydrogen. For reaction in two lengths of reaction tube, so that the reaction time was more

than doubled, and with cold and preheated methane, experimental acetylene conversions obtained could be described by a single function. It was not stated that a fixed hydrogen to methane ratio was used with their experimental work, although this was suggested by other comments. The function of methane conversion vs. enthalpy (per mol of methane) which was found, agreed well for the higher enthalpies (14 to 19 kJ g^{-1} mixture) with that calculated using their theory, but was 75% higher than that predicted at lower enthalpies (8 to 9 kJ g^{-1}). This was strange, as it would seem likely that the analysis would become more accurate as the temperatures over which the kinetic data were used approached those temperatures at which they were measured.

Anderson and Case relax one of the assumptions of their theory to explain this discrepancy - the assumption of very rapid complete mixing of reactants. They state that at low hydrogen enthalpies, slow mixing is obtained, and the portion of methane which is mixed with the hydrogen at first will react with a higher local enthalpy than the average, and so enhance the average acetylene composition above that predicted for very rapid mixing. A calculation using their predicted acetylene conversions for both a high enthalpy part of the methane feed and a balanced low enthalpy part shows no higher conversion for the total feed than that predicted for the feed with the mean enthalpy. Indeed, this would be expected generally because the relationship between methane conversion and enthalpy is almost a straight line. Anderson and Case associate poor mixing with low hydrogen enthalpy, whereas the reverse would be

expected. The hydrogen stream at higher enthalpies becomes highly viscous, and mixing of a cold, low viscosity gas stream with this high temperature, viscous stream is likely to become more difficult as the temperature of the latter is raised.

The theory of Anderson and Case also predicts that for reacting mixtures of hydrogen and methane where the initial mixed enthalpy corresponds to a temperature above 2000K, and more than 10% of the methane remains unreacted (not too high an enthalpy), then the temperature of the mixture will remain in the region 1700 to 2000K for contact times between 0.2 and 5 ms. This was found to be so, at least for high yield experiments, from measurement of the heat transfer during quenching, and making an energy balance over the quench device.

The theory of Plooster and Reed considers that heterogeneous equilibrium is attained in their apparatus, and they give the predicted acetylene concentrations if a particular reaction scheme involving the radicle C_2H is followed during rapid cooling of gas samples. Their experimental measurements were obtained from gas samples withdrawn through cooling probes of carefully chosen internal diameter (< 0.5 mm) at velocities of about 2.5 m s^{-1}. They obtained, by experiment, acetylene concentrations of 1 to 4 mol % at a pressure of 1 bar for temperatures from 2500 to 2900K (of the carbon tube). At a lower pressure, 0.25 bar, the concentration of acetylene showed a small increase from the higher pressure values, on average, but the values were more scattered. The predictions of the theory agreed to within about 20% with the experimental values. To test for equilibrium, about 5 mol % of

acetylene was added to the hydrogen flowing through the carbon tube. The samples showed the same acetylene concentration as before, indicating that some form of equilibrium prevailed in the gas. Plooster and Reed did not mention the flow rate of hydrogen fed, but indicated that a contact time with the tube of the order of 0.1 to 0.3s was calculated. It is disappointing that they apparently did not vary the hydrogen flow over a wide range. If the same concentrations had been obtained at any given temperature with differing hydrogen flows, solid-gas equilibrium would have been indicated.

Plooster and Reed restricted their calculations to the species H_2, H, C_2H, C_2H_2 and solid carbon. The more extensive calculations of Duff and Bauer indicate acetylene concentrations of 1.0 mol % at 2460K and 1 bar in equilibrium with graphite, and 3.0 mol % for a temperature of 2800K under the same conditions. These compare well with the experimental values of Plooster and Reed, of 0.9 mol % and 2.7, 3.4 mol % for 2480 and 2800K respectively at 1 bar. Since the C_2H concentrations was calculated by Duff and Bauer to be 0.5 mol % at 2800K (decreasing at temperatures below this), and according to the theory of Plooster and Reed, over 90% of this is expected to form acetylene, then their theory predicts an "improved" value of 3.0 + 0.5 = 3.5 mol % at 2800K. This appears to be still within Plooster and Reed's experimental error, so their theory is not disproved. Plooster and Reed indicated that some results at temperatures above 3000K and pressures of 1 bar were much lower than an extrapolation of the data taken at lower temperatures suggested. Using the extended

calculations of Duff and Bauer, the equilibrium concentration of acetylene rises to a maximum of 7 mol % at 3300K, whereas the C_2H concentration is calculated to be 8 mol % at 3300, rising to a maximum of 15 mol % at 3800K. Using Plooster and Reed's reaction scheme, a maximum concentration of about 19 mol % acetylene is predicted from a temperature of 3500K. A simple preservation of the acetylene present at higher temperatures appears preferable to Plooster and Reed's theory, on this basis.

Duff and Bauer's calculations show the same acetylene concentration at 2500K for pressures of 10, 1 and 0.1 bar-that is, 1.0 mol %. In contrast, the 2800K concentration dropped from 6.5 to 3.0 to 2.5 mol % for pressures of 10, 1 and 0.1 bar respectively. Experimental values from Plooster and Reed at 0.25 bar lay convincingly at 1.0 mol % acetylene for 2500K, and one point of 2.5 mol % was recorded for a temperature of 2800K. However the experimental values rose to 6.5 mol % at 2950K, and reportedly even higher above 3000K, whereas the maximum concentration at 0.25 bar from the work of Duff and Bauer is by interpolation from 4 to 5 mol % in equilibrium with solid carbon at 3100K. The theory of Plooster and Reed, using Duff and Bauer's calculations, predicts a concentration of 6 mol %, a figure which is close to the experimental findings and inside their range of scatter.

From the above discussion it appears that the assumption of a kinetic step from heterogeneous equilibrium by Plooster and Reed, and a specific kinetic step in particular, is unnecessary for the measurements at a pressure of 1 bar, and even undesirable. A simpler theory may be proposed. It is that heterogeneous

equilibrium is established in Plooster and Reed's apparatus, and at a pressure of 1 bar, the equilibrium concentration of acetylene is preserved on rapid cooling. The experimental results for a pressure of 0.25 bar disagree with the conclusions of this simpler theory for temperatures above 2800K, but do not disagree with the predictions from Plooster and Reed's theory.

Baddour and Iwasyk (7) applied Plooster and Reed's theory, changed to account for the presence of atomic and molecular carbon, and ignoring the formation of diacetylene, to their graphite arc reactor. For the experimental details, see chapter 3. In the initial experiments, hydrogen was fed into a carbon arc, and the gas sampled by cold probes. Their experiments show significant and consistent changes of acetylene concentration with change in hydrogen flow rate, or carbon feed rate. Thus a change in carbon to hydrogen ratio at a given pressure caused a change in acetylene concentration. Under the assumption that solid-gas equilibrium attained, no further degrees of freedom were available in the system, so the temperature was a dependent variable. This increases with increasing C/H ratio at a given pressure. The carbon feed was hot, and the hydrogen feed cold, so that the temperature would be expected to increase with increasing C/H ratio anyway, independent of the above equilibrium assumption. Quantitative information on the temperature was necessary to test the assumption, but this was not available.

As indicated before, the use of Duff and Bauer's calculated values for the C-H system in equilibrium with graphite gives a maximum of 7 mol % acetylene for a temperature of 3300K,

and if Plooster and Reed's reaction scheme is followed, a maximum acetylene concentration of 19 mol % is predicted, at 3500K. Each of these temperatures would be expected to be reached at some location in Baddour's reactor. In the reaction of graphite and hydrogen, concentrations from 2 to 26 mol % were found (7,8). These results disprove the simple preservation of acetylene from heterogeneous equilibrium theory for this reactor. The concentration of 26 mol % acetylene is larger than the 19 mol % expected as the highest concentration following Plooster and Reed's theory, so the latter is also disproved for this reactor.

Baddour and Blanchet (8) found an acetylene concentration of 52 mol % from rapid cooling of the gas in front of their carbon anode, when the reactor was fed with methane. They attempted to construct a theory based on specific irreversible chemical reactions i.e. reaction of atomic carbon with the hydrogen molecule to form acetylene, and the direct reaction of methane to acetylene and hydrogen. They predicted a concentration of from 40 to 47 mol % for temperatures of reaction from 2000 to 4000K, with the suggestion that higher concentrations were obtainable at higher temperatures. At 4000K, however, the reaction of methane would presumably be first of all concerned with breaking C-H bonds, after which the radicle would become indistinguishable from the other radicles present. It is thus doubtful whether their "temperatures of reaction" can be related to experiment.

The theory proposed by the author will now be tested. Since it does not rely on any specific starting material, it should apply to all the results discussed previously, except perhaps the Plooster

and Reed experiments, where a relatively long time was allowed for contact between gas and solid wall, and heterogeneous equilibrium is expected. The results of this study should constitute the most severe test, for these results cover a wider range of both C/H ratio and specific enthalpy than those measured from other studies. As mentioned before, the experimental C/H ratios were upper limits only of the true C/H ratio just before quenching, because of carbon deposit in the reactor, whereas the specific enthalpies were expected to be unbiased. From the observation that proportionately much less of the carbon fed was deposited in the reactor at small currents, and that the proportion deposited rose to about 20% for currents of 35A, the true C/H ratio would closely approximate the measured value at low currents (associated with low acetylene concentrations) and fall below as the current rose, to the extent of 20% at 35A. A close look at the measured acetylene concentrations does in fact reveal this behaviour. The small concentrations (0.7 to 5 mol %) corresponded well with those calculated, but higher concentrations (6.3, 7.5 mol %) were placed at much higher C/H values than those predicted at equilibrium. A reduction of about 20 to 25% would not account for this difference. Other experimental concentrations even higher than these lay in a region where the predicted acetylene concentrations were almost independent of C/H ratio, and so would be expected to agree with these predicted values irrespective of a substantial reduction of C/H ratio. Excellent agreement was found for these values (8.0, 10.2, 10.2 mol % points).

Experimental data from plasmatron studies with methane and hydrogen, on the other hand, are accurately placed with respect to C/H ratio, but their calculated specific enthalpy before quenching is an upper limit on the true value, because of heat transfer to the reaction tube. As wide tubes were used in all the plasmatron studies considered, this heat transfer is expected to be small. It is seen that most of the methane-hydrogen data have lower specific enthalpies than the range of calculations done in this study, and they show decreasing acetylene concentrations with decreasing temperatures at temperatures less than perhaps 1800K. This follows the behaviour of 'equilibrium' values of Duff and Bauer. The position of the 2000K isotherm was established by two hand calculations, using the composition from the Duff and Bauer calculations, and molar enthalpies from the JANAF tables. It can be seen that the plasmatron experimental values indicate a maximum in acetylene concentration at a temperature from 2000 to 2500K. A broad maximum from 1700 to 2500K is given by the equilibrium values.

A maximum acetylene concentration of 52 mol % was obtained by Baddour and Blanchet with the carbon arc fed with methane at a pressure of 1 bar. Lafond et al. (9) with a similar carbon arc reactor, obtained the same figure with a methane feed at a pressure of 0.5 bar. They also fed methane diluted with argon so that the partial pressure of methane was 0.25 bar, and obtained a wide maximum of about 52 mol % (argon free) over a range of measured C/H ratios. Their maximum experimental value was 55 mol % (argon free). These high values do not disprove the author's theory, as Duff and

Bauer's equilibrium calculations for the absence of solid carbon show a 55 mol % maximum in acetylene at 1700K for a pressure of 0.1 bar, a 55 mol % maximum at 1800K for 1 bar (and 50 mol % maximum at 2100K for 10 bar), all at an atomic C/H ratio of 1.

The theory of supercooled equilibrium with respect to graphite, followed by a preservation of species other than free radicles has been tested with respect to acetylene preservation, and the only observations disagreeing were the higher C/H data from the author's study. A look at the other stable molecules for which there is data, and also soot formation, will now be attempted. From the experimental measurements with the gas chromatograph in this study, any other stable molecules than acetylene and hydrogen were present, if at all, in concentrations below the limit of detection (0.1 mol %). The equilibrium calculations of Duff and Bauer predict a concentration of diacetylene, C_4H_2, of 0.13 mol % at a mass C/H = 1.2 and temperature 2500K, and the author's equilibrium calculations show that the diacetylene concentration falls below this for smaller C/H ratios at the same temperature. All other stable species (methane, ethylene, ethane) showed concentrations much less than 0.1 mol % for temperatures of 2500K and above. For higher C/H ratios (mass ratio=3) corresponding to the 10.2 mol % acetylene experimental runs, and at the same temperature (2800K), Duff and Bauer's calculations show 0.4 mol % diacetylene. This could easily have been missed in the one more accurate gas chromatograph analysis done on a sample from one of the runs. Generally, the limit of detection was about 0.5 mol % for gas chromatographic

analyses carried out in this work.

From 2 to 4 mass % of the carbon fed appeared as soot, in runs with C/H mass ratio from 1 to 1.5 and specific enthalpy 30 to 40 kJ g^{-1} at the reactor exit. This can be compared with 2.4 mass % of the carbon present at super-cooled equilibrium in free radicles for a 1.2 mass C/H ratio and a temperature of 2700K.

The work of Kozlov et al. with the plasmatron reactor fed with hydrogen and methane gives details of methane and ethylene concentrations in their product gas. The table below gives a comparison of four of their results with that predicted from Duff and Bauer's super-cooled equilibrium calculations.

Table 7.1

COMPARISON BETWEEN PLASMATRON REACTOR PRODUCT GAS CONCENTRATIONS AND THOSE AT SUPERCOOLED EQUILIBRIUM AT THE TEMPERATURE BEFORE QUENCHING

Mass C/H Ratio	Specific Enthalpy	Equilibrium Temperature	CH_4 mol %		C_2H_4 mol %		C_2H_6 mol %	
			Exp.	Est.	Exp.	Est.	Exp.	Est.
1.8	27.0kJg^{-1}	2700K	0.48	0.013	0.59	0.004	-	-
2.3	24.2kJg^{-1}	2600K	0.87	0.020	0.73	0.006	-	-
2.6	12.2kJg^{-1}	1700	29.2	0.3	1.07	0.7	0.14	0.01
2.3	4.8kJg^{-1}	1300	27.9	25	1.15	0.6	0.63	0.01

H_2 mol %		C_2H_2 mol %	
Exp.	Est.	Exp.	Est.
86.0	85	12.1	9.5
83.2	85	14.9	11
60.0	85	10.5	14
56.0	65	5.32	0.4

The estimates of both the equilibrium temperature and the concentrations at those temperatures involved interpolation. The temperatures represent upper limits of the true temperatures. Despite these drawbacks, some conclusions may be made concerning the comparisons. The concentrations of methane and ethylene found from the two higher enthalpy experiments are significantly higher (x 50) than those given by the author's theory. All the concentrations except that of ethane may be brought close to agreement with experiment with the "1700K" experiment if that temperature was dropped to 1500K. The "1300K" experiment shows a significantly low prediction of acetylene concentration. The experiment shows a value predicted for a temperature of 1500K for the same C/H ratio.

Allowing for inaccuracies mentioned above, the theory proposed by the author appears to successfully account for the major species in the plasmatron studies. The minor species, ethylene, ethane, (and methane at higher temperatures) whose concentrations are about 1 mol % or less show a disagreement. With methane and ethylene the experimental results can be explained by a partially completed reaction toward equilibrium concentrations as the temperature is lowered during the quench. A serious difficulty is found with ethane, for the maximum equilibrium concentration at any temperature and C/H ratio for a pressure of 1 bar is calculated to be only 0.01 mol %, and reactions must be directed toward equilibrium reaching a maximum concentration of 0.01 mol % if equilibrium was attained previously at any other temperature. The total concentration of ethane, propane, butane and larger hydrocarbons in the feed was 0.40 mol %

and 5.1 mol % for the third and fourth experiment respectively, which could account for the product concentrations of ethane, and perhaps all the discrepancies observed only in the minor components of the product gas, by some feed bypass.

It must be remembered that the calculated values of Duff and Bauer have been assumed to be correct equilibrium concentrations throughout this discussion. Some independent checks on the thermodynamic data do exist. In 1967, Clarke and Fox published a report (10) describing experiments which were designed to achieve equilibrium between a hydrocarbon gas and graphite for temperatures from 2600 to 2800K, and a pressure of 0.10 bar. They varied the starting C/H ratio of the gas and adjusted the graphite temperature for each C/H ratio so that no carbon transfer between gas and solid phase was measured over a period of minutes. The graphite temperature was measured with a pyrometer. Measured sublimation temperatures agreed with those calculated by Duff and Bauer (mass C/H ratios from 0.36 to 0.6) to within 50K, and were centred about the calculated line. The acetylene concentrations of the work of Plooster and Reed previously discussed can be cited as evidence supporting Duff and Bauer's calculations in the same limited temperature range.

7-B Particulate Carbon

B1 Relevant Experimental Observations

The radiation from the side of an arc struck on a 3.3 mm diameter graphite anode was measured in this study. Also, two methods were used to measure the arc radiation from a position 1 to 3 mm out.

from the ablating surface of the anode. The radiation will be related to that observed normal to the anode end surface through a quiet low current arc by Hattenburg (11) (effectively radiation from a 3800K blackbody). It was found with a thermopile that radiation from 45 and 50A arcs about 3 mm out from the anode was roughly 0.1 and 0.2 of the radiation from a 3800K blackbody. From the spectrograph measurements, roughly 0.1 of 3800K blackbody radiation was emitted from a 24A arc to the side from a position 1 mm in front of the anode. The shape of the optical density-wavelength curve, although near the low sensitivity spectral region of the photograph, was similar to the shape obtained from the calibration carbon arc. An upper limit of 7000K could be placed on the temperature of an equivalent blackbody radiator from a lower limit of 700 nm for the wavelength of the maximum intensity.

Clarke and Fox (10) found that with a graphite filament heated in hydrogen, the carbon found in hydrocarbon molecules formed from the reaction of graphite with hydrogen, was significantly less than the carbon lost from the filament for temperatures above 2700K up to the highest temperature measured, 3500K. The same authors also found in later work in vacuum (12) that when they heated a graphite filament to temperatures above 3400K by passing a current of electricity through the filament, an arc formed along its surface. It is calculated by this author that their filaments, 1.00 mm by 0.40 mm in section, had a resistance of only $2.5 \times 10^{-4}\ \Omega\ mm^{-1}$ of length, assuming an electrical resistivity of $1.0 \times 10^{-4}\ \Omega\ mm^{-1}$ for graphite at

3400K (13). If they used the maximum current which their system was capable of (100A), the corresponding voltage gradient along the filament would have been only 0.25V mm^{-1}. This in turn would require an equally low resistance path through the gas phase before appreciable arcing occurred. Clarke and Fox noted that the presence of hydrogen suppressed this tendency to arc, allowing arc-free experiments to be carried to a higher temperature.

In the reactor used in this study, several balances of carbon mass flows in and out of the reactor were attempted. The details are presented in Table 7.2 below.

Table 7.2

CARBON FLOW BALANCE OVER THE ARC REACTOR FOR CURRENTS OF 30 TO 35A AND HYDROGEN FLOW OF 18G H^{-1}

Run No.	67	80	81	83
Carbon feed rate, mean/g h^{-1}	17.5	26	27	27
Hydrogen " " /g h^{-1}	17.5	18.0	18.0	18.0
Average C/H mass ratio	1.0	1.45	1.5	1.5
Total carbon fed/g				
(a) $\int$ Rate.d(time)	6.5	4.07	4.35	5.3
(b) Approx. 1 rod used	-	3.96	4.1	-
Carbon found:-				
In acetylene	4.2	1.8	1.8	2.6
On exit tube	1.210	0.48	0.65 (chunk anode)	1.44
Carbon loose in chamber	0.045	negl.	0.13	negl.est.
In cooler and q tube (soot)	0.264	0.164	0.09	0.2 est.
Total found	5.72	2.37	2.67	4.2
Unaccounted for	0.8	1.7	1.7	1.1
% of carbon fed, missing	12%	42%	39%	21%

It can be seen that for all four runs, a significant proportion of the carbon fed to the arc could not be accounted for. The section of the reactor walls below the cathode was not measured for carbon deposit, since negligible deposit was observed by eye. The largest discrepancy above, a mass of 1.7g, would have been almost sufficient to close the reactor chamber off, had it been evenly spread over this lower section of wall. It was also noticed that from 10 to 50% higher gas flow was indicated by the product gas rotameter (likely error $\pm$ 15%) than was calculated from the measured inflow of hydrogen and the acetylene composition.

In 1969, Whittaker and Kintner presented a short report (14) describing a deposit formed on a flow tube opposite a heated piece of graphite in the tube, despite a gas flow through the tube of 5 to 10 m s^{-1}. The position of the deposit apparently changed little when flow velocities were increased to at least 50 m s^{-1} (pressure 1 to 12 mbar). Graphite was then heated in a vacuum (pressure $< 0.5 \mu$bar) with its surface covered by a double-walled enclosure with a small aperture in each wall so that the vapour could expand as a beam through the apertures. For temperatures above 2950K, scattering of a light beam (Tyndall effect) was observed in the vapour flow issuing from the apertures. Since this was attributed to colloidal sized particles of graphite in the vapour, an attempt was made to collect them on silicone grease. Examination under an electron microscope showed a density of $\sim 10^7$ particles mm^{-2} of collection area. Most of these corresponded to clusters of 10^4 to 10^5 carbon atoms (would

correspond to a cube of side 5 to 10 nm), with fewer (10^6 mm^{-2}) of about 50 nm in diameter and very few of 70 μm size. Some confusion was apparent in Whittaker and Kintner's article concerning this distribution, but it was understood that the above was what was meant. Most of the particles appeared to be angular cleavage fragments, and their electron diffraction pattern indicated that they were crystalline. It was argued that the crystallites could not have been formed by gas phase reaction in the time taken to reach the collection plate, and so were likely to have come directly from the graphite surface.

B2 Theory

It is proposed here that graphite crystallites are split off the anode of a carbon arc when the current density is sufficiently high, and control many of the properties of the carbon arc at high current density. The view that carbon particles could explain the radiation from the carbon arc has been held by Schmidt and Finkelnburg (15, 16) at one time, but the idea was rejected by Finkelnburg because of the difficulty of explaining blackbody temperatures of 6000K observed with the Beck arc.

Some of the consequences of this proposal will be discussed, and their possible influence on the operation of the reactor in this study will be suggested.

Bulk graphite has a work function (ionization potential) which is generally accepted to be about 4.6 eV. As the size of the piece of graphite is reduced, the work required to raise an electron from its thermodynamic state within the graphite to an

isolated state outside (ionization potential), is increased because of the attractive forces of the positive charge induced in the graphite particle. When the particle becomes small these attractive forces act over a shorter distance, and become significant. The problem can be treated by the method of image point charges, and Howard (17) presents a solution for spherical conducting particles, for single and multiple ionization. The effective ionization potential for a particle of radius "a" was given by

$$\phi_n = \phi + (e^2/2a)[2n - 5/4]$$

where ϕ = work function of bulk graphite,

ϕ_n = work function for removal of the nth electron,

e = charge of an electron,

and ne = charge on particle after removal of the electron in question.

Using numerical values, the expression becomes

$\phi_n = 4.6 + (1.44/2a)[2n - 5/4]$eV, with "a" in units of nanometers. The ϕ_n are given in table 7.3 for spherical particles of conducting carbon of diameter

2a = 1, 3, 10 and 50 nm (10 to 500 Å).

An arc is required to be electrically neutral, and so the presence of mobile electrons requires also the presence of positively charged particles (generally ions). The number of these generated in the arc per unit of time depends upon their loss from hotter parts of the arc to cooler parts, and on their loss to the cathode - that is by carrying some of the electrical current. The rate of loss of positive particles in turn is influenced by

their mobility in an electric field, and their diffusion velocity under a concentration gradient.

Table 7.3

EFFECTIVE ELECTRONIC WORK FUNCTIONS FOR SPHERICAL, ELECTRICALLY CONDUCTING GRAPHITE PARTICLES OF SMALL SIZE

Particle diameter/ nm	1	3	10	50
n, no. of electronic charges after ionisation				
1	5.7	5.0	4.7	4.6
2	8.6	5.9	5.0	
3	11.4	7.4	5.3	
4		7.8	5.6	
5		8.8	5.9	4.9
10		13.6	7.3	5.1
20			10.2	5.7
50				7.4
100				10.4

It is seen from table 7.3 that a possible consequence of the presence of carbon particles in the arc is their acquisition of positive charges. This would make them a competitor with small molecules for the ionization reaction. A likely list of ions for the carbon-hydrogen system, which have been observed in mass spectrometry, together with their first ionization potentials, are C_3H_7 7.9eV, C_3H_5 8.1eV, C_3H_3 8.25eV, C_4H_5 8.7eV, C_2H_3 9.45eV, C_3H_6 9.73eV, C_2H_5 9.8eV, CH_3 9.86eV etc., with

C 11.26eV, C_2 12.0eV, H 13.5eV, and H_2 15.6eV. The ion $C_3H_3^+$ is found in flames as a major positive hydrocarbon ion. Some of these hydrocarbon ions may be expected if the gas was in thermal equilibrium with the solid carbon, but at normal arc temperatures (8000 to 12000K) it is expected that only C^+, C_2^+ and H^+ will be present. Thus the presence of (evaporating) carbon particles would perhaps be associated with gaseous ions of lower ionization potential than would be otherwise present in an arc, since thermal equilibrium between the gas molecules and the carbon particles is likely. It appears that should carbon particles be present, they would be favourable contenders for electron removal, for ionization potentials below about 8eV.

The mobility of such positively charged particles is expected to be much lower than that of the molecular ions, and thus they would carry a smaller fraction of the current. The diffusion of such solid particles out of the arc is also expected to be negligible compared to the diffusion of molecular ions. Finally, multiply-charged particles are possible without the ionization potential rising above 8eV. Thus the required rate of production of charged carbon particles needed for arc operation would be expected to be well below the normal required rate for molecular ions.

If carbon particles are present in the carbon arc just in front of the anode, and explain the continuous radiation, then it appears that they can exist in an arc over 10 mm from the anode when a high current density is applied to the anode (16). If the particles reached the cathode before they vapourised, one would expect a rapid build-up of carbon on the electrodes, indeed

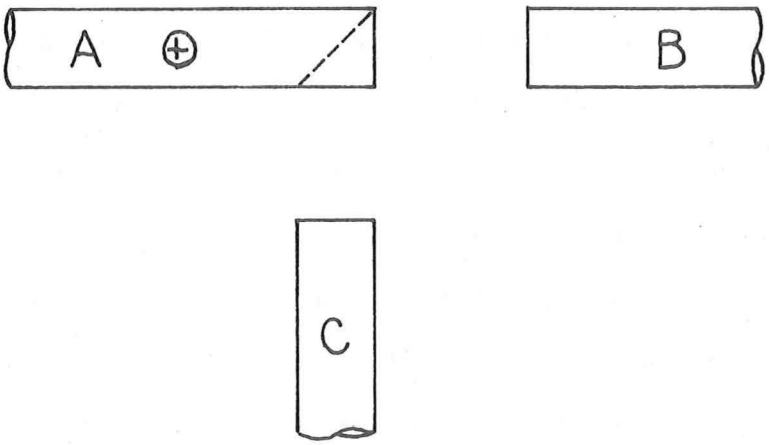


FIGURE 7.2 THE THREE CARBONS OF FINKELNBURG (15)

what has been observed in these experimental studies. Finkelnburg described some simple experiments with three carbon electrodes. His arrangement was as in figure 7.2, with A as anode, and B and C either cathode or isolated electrically. When he operated a high current arc between A and cathode B, with C isolated, a large deposition occurred on B, but none on C. If on the other hand C was the cathode, and B was isolated, but situated in the "positive flame", a large deposition was found on C, and a smaller one on B. From the experiment, it appears that most of the carbon followed the arc, and presumably was positively charged. However, some could deposit on a very hot electrically isolated surface.

Finkelnburg showed photographs of the "mushroom" deposits formed on cathodes in his book on carbon arcs (15), and they looked very similar to the deposits found in this study. He reported that up to 40% of the carbon ablated from the anode was found as a mushroom deposit on the cathode. It was found that the carbon deposited on the hottest part of the cathode (the part carrying most current), making doubtful any possible mechanism of condensation of neutral carbon molecules. Finkelnburg found a deposition rate of up to 5×10^{-4} g of carbon $A^{-1}s^{-1}$. Finkelnburg assumed that the current carried in the opposite direction to the electron flow was carried by C_2^+ ions, and estimated that 5% of the total current was carried by these ions. Using Faraday's law, he calculated that only 1.3×10^{-5} g of carbon per ampere-second of total current could be deposited in this fashion, i.e. 4% of that found. If carbon particles

carried the major part of the 'positive' current, on the other hand, presumably less of the total current would be carried by positive charges. The number of carbon atoms for each positive charge on such particles (up to 8eV ionization potential) would vary from 50 C atoms/electronic charge for a diameter of 1 nm, to 6500 C atoms/electronic charge for a diameter of 50 nm. Thus no difficulty arises in explaining the likely lower limit for the mass transferred per charge transferred by positive carriers, required by Finkelnburg's measurements (25 C atoms/electronic charge).

B3 Use of the theory to construct a model of reactor operation

The three-carbon experiment of Finkelnburg can be thought analogous to the situation in the reactor of this study. The cathode was perpendicular to the anode and somewhat removed from the flow of material from the anode. Significant build-up often occurred on the cathode and less occurred on the cathode and less occurred on the hot electrically isolated exit tube. If the presence of carbon particles in the arc is postulated, then some at least of the carbon deposition on both exit tube and cathode will have been due to deposition of these particles. It is likely also that the unexplained carbon loss, together with a measured product gas flow rate which was higher than calculated, could be explained by the loss of very small particles of carbon with the product stream. These would have had to be very small (certainly less than 0.5 μm) to avoid settling in the cooler chamber, or to avoid being caught in the tightly-packed fibre-glass filter. The product gas flame was brightly luminous, with measured concentrations

of only 5 mol % acetylene. A strongly aromatic smell was noticed in the cooling chamber after most runs when it was cleaned with a brush. If it is supposed that all the deposit on the exit tube, together with the carbon unaccounted for, was present as carbon particles in the arc, then the particles would have represented 29%, 54%, 54%, and 48% of the carbon fed for the four runs treated before. The first run had a significantly lower carbon ablation rate than the others, which were run under almost identical conditions. Having established some confidence in the theory that carbon particles, as well as molecules, are ablated from the anode of a high current carbon arc, some rather tenuous though testable consequences will be suggested to explain arc behaviour and acetylene yields in this experimental study.

Arc behaviour

Arcs with currents below about 20A will be discussed first. It is suggested that the presence of carbon particles is not important in these arcs and that the small number of particles splitting off the anode are vaporised before travelling very far along the arc. It was suggested in chapter 5 that the low current arc operated in two modes, a free-standing mode and wall-hugging mode. As discussed there, the wall-hugging arc would have had to be of higher voltage than the free-standing arc to satisfactorily explain the sudden drop in voltage observed with increased cathode hydrogen flow. As can be seen from figure 7.1, the mean enthalpy of the flow passing out from the exit corresponded to temperatures from 2000 to 3000K. The exit tube was presumably cooler than this as the gas stream was cooling to the wall.

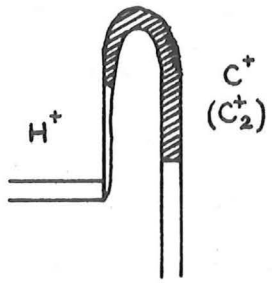
If a temperature of 2900K is taken as the temperature at which graphite particles begin to split off graphite, then it would appear that the arc would need to exist in close proximity to the exit wall for some time before causing the emission of graphite particles, to make the route more attractive. It is difficult to state the likelihood that graphite particles would be emitted above 2900K with only the surface layer heated, since the instances given above in the literature were either heated from within the solid, or were close to the sublimation temperature.

Another possible, and more probable explanation of the apparent dichotomy of low current arc operation (stability at both 90-120V and 150-170V) lies with the type of ions assumed to be in the arc. It was stated before that at normal arc temperatures (8000-12000K), only C^+, C_2^+ and H^+ are likely to be present. The carbon atom and molecule have a lower ionization potential than the hydrogen atom (C 11.26 eV, C_2 12.0 eV, H 13.5 eV), but more important than this, have a much smaller diffusion rate because of their larger mass. With a long arc, the creation of positive ions at any section in the arc almost balances their loss by diffusion to the arc boundary. Thus fewer ions would need to be created per unit time with an arc using C^+ charge carriers than one using H^+ carriers. One would expect the voltage gradient along the arc to be smaller for the arc containing carbon. The convection (forced and natural) of the carbon vapour upwards from the anode would thus create a favourable lower-voltage-gradient path for the arc forward of the anode. The question then arises as to where the arc bends from this path to attach to the cathodes.

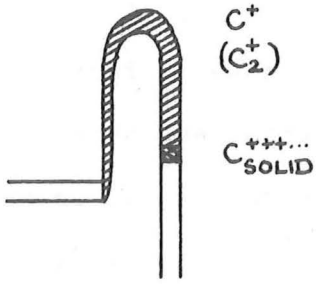
It is suggested that this will depend on the overall flow of hydrogen through the arc chamber and the local flow velocities, influenced by wall shape. The 150 to 170V arc voltage was observed with currents less than 15A - that is with low ablation rates of carbon. It is proposed that the arc was sufficiently long to lose this carbon from it, resulting in a pure hydrogen arc closer to the cathode, with a resultant higher voltage. For currents above 15A, but perhaps not above 30A, sufficient carbon may have been introduced to allow operation with atomic or molecular carbon ions almost up to the cathode. Figure 7.3 summarises this concept.

This mechanism allows for operation with all voltages between the maximum and minimum observed. The stable maximum voltage may have been due to confinement of the arc by the exit tube, as outlined before. Any small disturbance at the cathode such as a stronger blowing of the arc into the centre of the chamber would have the effect of making migration of C^+ to the cathodes easier, thus lowering the voltage and raising the current, at a given setting of the ballast resistor. More current would ablate more carbon, thus making the new arc state stable. This latter corresponds to what was observed. If the anode tip was upstream of the cathodes, the chemical composition of the gas in the gap between anode and cathodes would be likely to change rapidly perhaps causing the fluctuations which were observed.

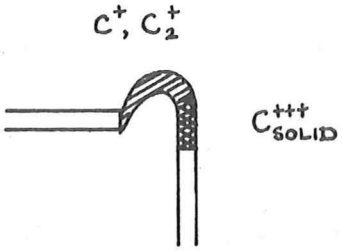
Larger currents (up to 35A or higher) were associated with voltages from 80 to 90V, and it is proposed that the positive charge carriers in these arcs were carbon particles over a



I < 15A, 150 TO 170V



15A ≤ I ≤ 20A, 90 TO 120V



20A < I < 35A, 70 TO 80V

FIGURE 7·3 PROPOSED MECHANISM FOR LOW CURRENT ARC

section of the arc near to the anode, and atomic or molecular carbon for the remainder, after the solid carbon had vaporised (see figure 7.3). Larger currents again (greater than 35A) were seen to be associated with a "cross" configuration. The analysis of Maecker (18) of the pinch effect of the self-magnetic field about an electrode gives the resultant jet velocity in front of the electrode by

$$v^2_{limit} = \frac{\mu_e I^2}{2\rho\pi^2 r_a^2}$$

where v_{limit} = velocity induced along the centreline

I = current to the electrode

μ_e = magnetic permeability

ρ = density of the gas

r_a = radius of the arc attachment to the electrode.

For the run which is shown in the frontispiece, with a red jet apparent from the side cathode, the total current was 45A (with a 65 to 70V arc voltage). If the current was evenly distributed, each cathode would have carried 15A. It is assumed that the temperature of the gas in front of the cathode was 8000K, and was largely hydrogen (arcs at 1 bar pressure are commonly only 10^{-4} ionized, so the positive species could still be carbon). The magnetic permeability was taken to be that of vacuum, and r_a was taken to be the radius of the white spot appearing on the opposite cathode in the photograph (equal to the radius of the red streak out from the side cathode) i.e. 0.3 mm radius.

Using the values given above, the velocity along the centreline of the jet was calculated to be 10 m s^{-1}.

This tranverse velocity to the main flow through the reactor can be compared with the velocity of the main flow, which issued from the annulus about the anode at from 2 to 6 m s^{-1} (room temperature), spread out and heated until the average flow was about 4000K (see chapter 8). The average velocity through the chamber was then calculated to be from 5 to 15 m s^{-1}. Superimposed on this flow was the vapour jet from the anode. Assuming that at 50A current, 50% of the ablating carbon was molecular, with a mean molecular weight of 24, and a temperature of 5000K, a velocity of about 25 m s^{-1} was calculated for the mass leaving the anode.

These calculations suggest an arc mechanism at higher currents which is controlled by the cathode and anode jets. From the red colour of the jet from the side cathode in the frontispiece, it appears that the cathode jet consisted almost solely of hydrogen, and that the velocity was sufficient to react and/or sweep away migrating carbon particles from the cathode area. It is suggested that the carbon particles, when present in the arc, kept the surrounding gas relatively cool (cf. Johnson's measurements of 5200K for the electronic temperature of the hydrogen atom close to a carbon anode) by evaporation and the requirement of lower ionization potentials. Thus indication of a strongly excited H_α line of the Balmer series (identified with the red colour) suggests the absence of carbon particles.

If by some means a small layer of carbon was built up on the cathode tips, a high temperature would have been reached over

the extent of the layer instead of at a much restricted arc "foot" as with tungsten, because of the much reduced thermal conductivity of carbon compared to tungsten. Thus electron emission would be expected to spread over the entire tip, losing the cathode jet, which relies on a small arc diameter. The way would then be open for the easier migration of carbon molecules and particles (ionized) by the shortest route to the cathodes, resulting in heavy carbon deposit. The absence of any clearly defined arc path in the last coloured photograph, taken when appreciable deposit had formed on the cathodes, suggests that the current path was spread over almost the whole of the chamber volume. The effectiveness of the cathode hydrogen flow in preventing carbon deposit is seen to be in preventing the initial small carbon deposit, rather than in preventing the arrival of carbon particles directly. The initial carbon deposit, which was observed to form slowly, was likely to have been caused by migration of molecular or atomic carbon ions to the cathodes. A pure hydrogen stream enveloping the cathodes would cause very efficient cooling of the cathode tips because of a high translational thermal conductivity, enhanced by dissociation - recombination for cathode temperatures above 2000K. This would ensure that the electron emission was restricted to a small area, creating the cathode jet. The supply of pure hydrogen to this jet just beside the tip would prevent the induction of carbon bearing gases from the arc chamber by supplying sufficient hydrogen for the jet, and for buffering the intake of the jet from the surrounding gas. The dilution of carbon

species in the arc by the hydrogen jet is suggested as the reason for negligible deposit when the cathode hydrogen flow was sufficient. Too high flows may cause entrainment, eventually causing carbon deposit.

The breaking down of the "cross" configuration and the rapid carbon build-up which followed, were accompanied by a gradual drop in voltage to 50 or 55V, and the disappearance of any red colour in front of the cathodes. The voltage drop is explained by the presence of carbon particles, according to the above theory, and it is suggested that the gas about the cathode was not hot enough to give Balmer radiation.

The achieving of gas-phase chemical equilibrium

It was estimated before in this chapter that for 35A arcs, about 50% of the carbon fed may be present as finely dispersed solid or deposited on the exit tube as the mass stream leaves the reactor. Thus the gas-phase carbon to hydrogen ratio at this position would have been only half what was measured in the feed to the reactor. As can be seen on figure 7.1, this correction to the higher current results brings them into agreement with the "frozen equilibrium" predictions, and with the plasmatron results. The 10.2 mol % acetylene points remain in agreement with this adjustment, for the predicted 10% lines are at constant enthalpy over the C/H range in question.

If the gas phase achieved chemical equilibrium by the time it left the reactor, it is pertinent to consider how. The average gas velocity through the chamber was calculated to be from 5 to 15 m s^{-1}, so that for a reactor chamber length of about 40 mm, the

average residence time was from 3 to 8 ms. From Anderson and Case's kinetic analysis, the gas phase reaction he considered was complete in times much less than 1 ms for temperatures above 1800K. It is suggested here that mixing of the reactants was the limiting step as appeared to be the case also with the plasmatron studies. The mixing problem is seen to be the mixing of the stream of carbon directed toward the exit, with the surrounding hydrogen. With higher currents and consequently higher rates of evolution of the carbon vapour, the mixing would have to become more rapid to be effective. Fortunately the cathode jet velocities are predicted to rise also, providing a mixing action.

The acetylene concentrations measured in this study supported the "frozen gas-phase equilibrium theory", but also some support was found for the proposed existence of small carbon fragments in the gas flow through the reactor. This appears to be contradictory, for one would expect gas-solid equilibrium to follow easily from the presence of many solid particles, well distributed in the gas phase. If both hypotheses prove satisfactory, then one possible conclusion is that the chemical properties of the carbon fragments are significantly different from that of graphite. If their sublimation temperature was lowered to below the experimental values, one would see a gas phase equilibrium (with vaporising particles) as being a "supercooled" equilibrium with respect to graphite, as has been done. Thus some limits on the acetylene concentration obtainable would be imposed by the new gas-solid equilibrium, when it was reached at

a lower temperature. The fact that concentrations of acetylene as high as 55 mol % were obtained with a high current arc system, that is, approximately equal to the maximum predicted under the frozen gas-phase equilibrium theory (needing gas-phase equilibrium at 1800-1900K, C/H mass = 12), would then need a change in sublimation temperature of about 1500K, which is unlikely. The alternative is that proposed before, a slow chemical reaction between gas phase and dispersed solid.

Anode ablation

It was suggested in chapter 3 that the energy balance over the anode tip determined the ablation rate. This was based on the assumption that the arc behaviour around the anode was independent of the rest of the arc, an assumption commonly made in developing the theory of arcs. For example, see Ecker's treatment (19). The plot made of anode erosion rate versus current through the anode was thought significant in this respect. In this experimental work, the length of the arc and consequently the arc voltage were observed to change to a large extent for any given current. This was in contrast to other high current carbon arc experiments seen reported by this author, where the arc voltage was a single function of arc current. Operation in a still gas, or operation with a very short electrode-electrode gap appeared to cause this reproducible dependence of arc voltage on current. Consequently Finkelnburg and others, believing that the anode phenomenon was related to energy dissipation in the arc successfully correlated the anode ablation rate with arc power. With the experimental data reported here, a correlation between

arc power and ablation rate was attempted, but no clear pattern emerged. On the other hand, close reproducibility was obtained about a single line when carbon ablation rate was plotted against the arc current.

If an energy dissipation at the anode tip was wholly responsible for the ablation, the energy dissipation must have been a single function of the current, and so the voltage drop over the important part of the anode tip region must also have been a single function of current. The ablation rate was independent of the hydrogen flow past the anode over the limited range of flows used. If an energy dissipation mechanism operated, then the cooling of the anode by the hydrogen flows cannot have changed significantly with flow rate. Ablation rates taken near the beginning of a run, before the walls reached steady state temperatures, also were found to lie close to the same line. In the design of the reactor, reradiation from the arc chamber walls was thought to be important for anode ablation, but with the anode at a temperature of about 4000K, and the walls at 2000K, only $(1/2)^4$ or 1/16th reradiation is calculated. Since anode radiation was only part of the heat transfer from the hot tip, ablation was regarded as being also independent of the condition of the rest of the arc chamber. Two exceptions to the well correlated behaviour of the ablation rate against current were reported in chapter 6. Both were at a high voltage of about 155V, and showed an ablation rate of about four times that given by lower voltage results at the same current. It was shown in chapter 5 that over a certain range of current above about 20A,

thin walls appeared on the tip of the anode and broke away. The 155V arcs were limited to currents less than 15A, with normally very little ablation of carbon. The two exceptions are interpreted as the establishing of a low current arc while the anode still retained its thin walls. These would be ablated rapidly but evenly with a low current, from their top, causing the illusion that the complete rod was being ablated at that rate.

Anode Hissing

Some discussion on the "hissing" phenomenon at the anode of a high current carbon arc may be appropriate here, for the rapidly moving terminus of the arc associated with the phenomenon could provide excellent mixing of carbon and hydrogen. It is not certain whether such contraction of the arc and movements of the contraction did occur in the reactor operated in this study, for no sound was heard from outside the reactor. A hissing sound was heard at a low current during one run, but this was thought to be associated with one cathode. Finkelnburg observed both a high frequency of current and voltage fluctuations (up to 80 kH) and a low frequency (from 1 to 3 kH). These oscillations corresponded to fine and gross behaviour of the arc foot on the anode, as determined by high speed photographs. The arc foot was observed to move periodically across the anode face away from the cathode (short arc) corresponding to the lower frequency above, and reignite after extinguishing at the farthest rim. Within the arc foot, a microspot with an apparent current density of 500A mm^{-2} was seen to rotate very rapidly corresponding to the high frequencies above.

Finkelnburg suggested that the more rapid movements of the microspot were due to local evaporation, and that the microspot was held within the slowly moving "foot" by inertia of the arc column. He did not attempt to explain the periodic slow movement. It was observed with the anode held both horizontally and vertically, and with the cathode directed at the anode face. Finkelnburg reported short quiet periods between hissing, and observed that the tendency to hiss diminished with increase in arc length. It is suggested here that the magnetically pumped cathode jet swept the arc across the anode face in the case of the hard core carbon which formed little crater, but could not move the Beck arc attachment, and so could not contract it, because of the sheltering of the walls of the deep crater formed. Under this hypothesis, contraction of the arc at the anode of the reactor in this study is unlikely, for at high currents the anode tip was well below the cathode jet streams. It is likely that hissing would not be observed for an arc in such a configuration, and if one takes the microspot behaviour to be dependent on the occurrence of the larger scale contraction, the microspot would also not occur.

Finally in this chapter an unrelated topic will be dealt with. Drops of metallic substance, assumed to be tungsten, were found above the cathodes and lying in a "frozen pool" in the crater on the anode rod, after the tungsten cathodes were heated to melting point. As no tungsten was found on the chamber floor or on the walls around the anode, it is suggested that the material migrated along the arc,somehow acquiring a negative charge to do this.

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EVALUATION FOR ACETYLENE PRODUCTION AND ECONOMIC PROJECTIONS

CHAPTER 8

In this chapter, those aspects of the results relating to the commercial production of acetylene will be discussed, and some suggestions concerning larger reactors and the use of coal as a raw material, will be made. The model developed in the last chapter will be used without further testing, although further tests are obviously needed (for example an electronmicrograph of any deposit on a plate exposed to the product stream).

8.1 Concentrations and yield of acetylene

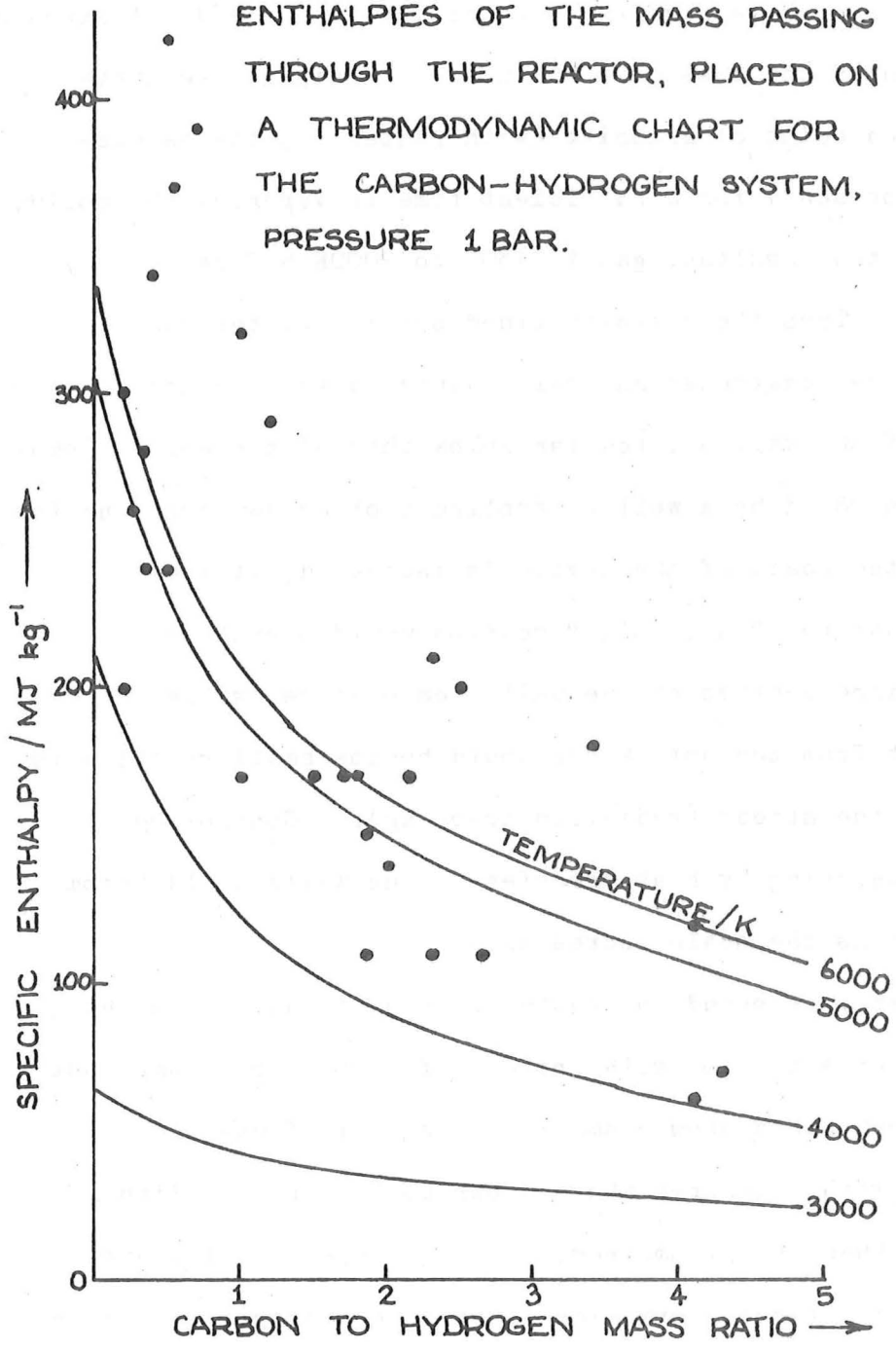
In the experiments reported in this study, a maximum acetylene concentration of about 12 mol %, and a (separate) maximum conversion of carbon to carbon in acetylene of 65%, was found. With higher carbon flows into the reactor than that corresponding to the above yield, the conversion to acetylene decreased until only 20% conversion was achieved at the highest carbon to hydrogen flow used. It can be seen from the acetylene concentration vs. C/H ratio graphs that data for different hydrogen flows followed a single pattern at the lower C/H ratios. The fact that the experimental concentration obtainable was a single function of the C/H ratio only for low C/H ratios, can be seen to agree with the predictions of the author's "equilibrium in the gas phase only" theory. Referring to the enthalpy - C/H ratio chart presented in the last chapter, it can be seen that the acetylene concentrations shown there are strongly dependent on the C/H ratio for small C/H ratios, and at the same time almost independent of the gas enthalpy.

Thus the uncontrolled variation in exit enthalpy in the experiments would, it is predicted, have little influence on the acetylene concentrations obtained, and these concentrations would approximate a single function of the C/H ratio. On the other hand, at higher C/H ratios it is predicted (from the chart) that the acetylene concentration is strongly dependent on the enthalpy and almost independent of the C/H ratio. Since the enthalpy was not controlled in the experiments one would expect much more scatter in the acetylene concentrations obtained at higher C/H ratios, which indeed was the case. The low overall conversions at high measured C/H ratios cannot however be attributed exclusively to high specific enthalpies, as is suggested by the chart in chapter 7. If it is taken into account that about 50% of the carbon fed remained in the solid phase, then the correct experimental gas phase states lay on a part of the enthalpy-C/H chart where the constant acetylene concentration lines were almost vertical. The acetylene concentrations were then limited by the gas phase C/H ratio, or the amount of carbon vaporised into the gase phase. However if the C/H ratio were increased by more vaporisation of the dispersed particles, it is expected that no higher concentrations of acetylene would result unless the enthalpy of the gas before quenching was also reduced. If both of these measures were achieved, concentrations of 25 mol % acetylene would be expected from the current and hydrogen flow settings which achieved 10 to 11 mol % in the experiments reported here. Concentrations of 50 mol % acetylene with high conversions may eventually be possible.

To achieve these higher concentrations and yields it appears necessary to hold the gas-solid mixture at a temperature above the sublimation point of graphite (with respect to the carbon-hydrogen gas present) for a sufficient time to vaporise the solid, and then cool the resultant gas to 1800 to 2000K before quickly quenching it. Thus the graphite-lined section of the reactor would have to be lengthened and well insulated to maintain the temperature of the wall not too far below that of the gas. Downstream of this would be a well controlled cooling section, and the quench. As the scale of the device is increased, it is anticipated that the "vaporising" section would operate more effectively, irrespective of the wall temperature, since the radiation lost from the hot carbon would become small relative to the energy in the stream (radiation trapping). Controlled cooling and quenching by heat transfer to the walls would become more difficult as the scale increased.

The theory proposed in chapter 7 predicts almost no change of acetylene concentration with pressure from 0.1 to 10 bar, but plasmatron experiments show a small falling-off of acetylene concentration with pressures above 1 bar up to 6 bar. With arc devices other than the plasmatron, which can operate at 1 bar without significant soot formation, a drop in pressure to 0.1 or 0.2 bar apparently much reduced soot formation, and increased acetylene formation. It is suggested that these problems lie with lack of control over temperatures (cold walls), poor mixing etc. which leave regions of high carbon concentrations and greater than average temperatures. The radicles present in

FIGURE 8·1 ESTIMATED UPPER ENTHALPIES OF THE MASS PASSING THROUGH THE REACTOR, PLACED ON A THERMODYNAMIC CHART FOR THE CARBON–HYDROGEN SYSTEM, PRESSURE 1 BAR.



these regions may form soot more readily at higher pressures. An alternative idea is that the acetylene which does form, decomposes to soot and hydrogen more quickly at higher pressures. Whatever the reason, lower pressure may be needed to achieve higher concentrations and conversions in the reactor of this study.

8.2 Energy use

The minimum energy required in this work to produce a unit mass of acetylene was 130 kwh (kg acetylene)$^{-1}$, compared to about 11 kwh kg^{-1} required commercially. It can be seen from figure 8.1 that the estimated maximum mean enthalpy (see Appendix 4) of the total mass flow through the reactor most often corresponded to temperatures of 5000K or greater. These high enthalpies (100 to 400 kJ g^{-1}) should be unnecessary, according to the model developed previously, which requires enthalpies of only about 40 kJ g^{-1} to fully vaporise the carbon at a low C/H ratio, or 20 kJ g^{-1} at very high C/H ratios. There appears no reason why larger reactors could not be run effectively with these lower maximum enthalpies, as the heat transfer to the walls by both convection and radiation transfer is expected to be much smaller per unit mass of throughput. It was noticed that the lowest maximum enthalpies obtained with the small reactor for any given C/H ratio were those with the highest mass throughput. Since a considerable increase in throughput is expected to be possible before difficulties with arc operation occur, a closer approach to the lower enthalpies is probable even with the present reactor.

When these low 'target' enthalpies are related to unit mass of acetylene produced, it is found that for a 90% conversion of carbon, 40 kJ per gram of mixture with mass C/H = 1 corresponds to 24 kwh (kg acetylene)$^{-1}$. Likewise, 20 kJ per gram of mixture with mass C/H $\gg$ 1 corresponds to about 6 kwh kg^{-1}. Thus it appears that to reduce the energy consumption, the vaporisation step for the entrained solid would have to be carried out at the highest possible C/H ratio. If it was not desirable to quench at this high C/H ratio because of low yield, it would be convenient to mix with it a stream with lower C/H ratio and lower enthalpy. By this means both the average C/H ratio and the average enthalpy before quench could be closely controlled. Suitable streams could consist of hydrogen, methane or heavier hydrocarbons, or particles of high volatile coal. The gas streams could be at room temperature or be preheated to a furnace temperature to save electrical energy should this be more costly than chemical fuel energy.

Effect of Scale

Some idea of the penalty paid in energy use by operating the anode on the small scale of this study, may be obtained by considering some of the energy flows to and from the anode tip. In 1937, Mason suggested that the anode voltage drop of a low current carbon arc was about 20V (1). Finkelnburg (2) on the other hand, stated that the anode drop of a high current carbon arc was about 30V, based on probe measurements and on the assumption of a contact potential between probe and plasma of only one or two volts. A value of 20V will be used here. The energy which is dissipated in a small region about the front face of the anode

is given by $I(Va + \phi)$, in watts,

where I = current, A,

Va = anode voltage drop, (20V),

ϕ = graphite work function, (4.6V).

This energy dissipation is then calculated as 490W at 20A and 1250W at 50A. The proportion of this energy dissipation which is used for carbon vaporisation at the anode can then be calculated, using the measured ablation rates, and the assumptions that 100% and 50% of the carbon ablated is vaporised at currents of 20 and 50A respectively. The enthalpy change of graphite from room temperature, 1 bar, to its sublimation temperature, 1 bar, was taken as 8.3 kJ g^{-1}. A value of 23.3 kJ g^{-1} was also assumed for the enthalpy of vaporisation of graphite at a pressure of 1 bar (from the calculations discussed in chapter 7 on the carbon-hydrogen system). The calculated energy requirements for vaporisation are set out in table 8.1.

It is seen that very low utilisation of the energy available from the arc mechanism is obtained with the small anode. From the photographs taken of the anode during operation, the very hot section of the anode appeared to extend only about one diameter back from the tip, showing that heat transfer from the side of the anode was much more important than heat transfer by conduction back along the anode. It was estimated by the Reynold's flow method of Spalding (3), using enthalpy as a potential for heat transfer, that the convective heat transfer to the hydrogen from the side of the anode was about the same size as that by radiation. Together, these two modes could

account for about 800W from a 5 mm length of anode assumed to be at an average temperature of 3500K, thus explaining the loss of most of the energy input to the anode. The radiation loss from the front face is expected to be reduced from that calculated in chapter 3, because of reradiation back from carbon particles in the gas phase. Thus the net radiation loss if expected to be less than 100W for the 3.3 mm diameter anode.

TABLE 8.1

ESTIMATED USE OF THE ENERGY DISSIPATED

AT 3.3 MM ANODE IN VAPORISATION

Measured:		
Current	20A	50A
Ablation rate	8 g h^{-1}	53 g h^{-1}
Estimated:		
Power dissipated at anode	490W	1250W
Heating of graphite to sublimation temperature	18W	120W
Assumed fraction vaporised	100%	50%
Power for vaporisation	52W	170W
Fraction of power dissipated usefully employed in vaporisation of carbon	14%	22%

The size of anode can be seen to be of importance in the efficiency of energy utilisation at the anode. The heat transfer to the side of the anode is related to the area of the cylindrical surface of the anode, and to a first approximation for any given

feed velocity etc., can be said to have a constant value per unit length of perimeter, no matter what the size of anode. For any given velocity of the anode, the throughput of carbon is directly proportional to the cross-sectional area, i.e. to D^2, where D = diameter of anode. Thus the heat transfer to the side of the anode increases as D, whereas the throughput increases as D^2, as D increases. The energy losses to the side per unit of carbon feed thus change as 1/D as D is increased. For example, when D = 3.3 mm, these losses were found to be approximately $900W/53\ g\ h^{-1} = 60\ kJ\ g^{-1}$ for a velocity of feed of 1.1 mm s^{-1} (s.g. 1.5.) (The 900W term was obtained by making an energy balance over the ablating surface to find the conduction back into the anode, and by making a further energy balance over a length of anode from just inside the ablating surface, to where the conduction term is unimportant, or alternatively making a single energy balance over both regions.) For an anode ten times the diameter i.e. D = 33 mm, these losses should reduce to 6 kJ g^{-1}, which is not large compared to the energy required to heat and vaporise the carbon anode ($8.3 + 23.3 = 31.6\ kJ\ g^{-1}$). From this argument, a reactor similar to the one described in this thesis but ten times in linear dimension, would ablate 5.3 kg h^{-1} at a current of 1300A or 100 times the carbon for 25 times the current.

One can test this scale-up procedure against the ablation rates found by Baddour and Iwasyk (4) for a graphite anode twice the size of the one used in this study, operated in hydrogen flowing at about the same velocity in the same direction.

For an anode velocity of 1.1 mm s^{-1}, they found an ablation rate of 190 g h^{-1} with a current of about 150A (an arc voltage of 50V was assumed by this author). The scale-up procedure predicts 140A for the same conditions, which is considered to be within the errors made in assuming the value of arc voltage.

From similar arguments, it will be seen below that with a larger reactor, the energy losses through the walls are similarly reduced, on a mass throughput basis. According to the theory in chapter 7, it was required that about 85% of the arc power be taken from the mass passing through the small reactor before the desired specific enthalpy was obtained, and appreciable acetylene was formed. With a larger reactor mentioned above, capable of causing the phase change $C_s \rightarrow C_{gas}$ with presumably much lower power dissipation per unit throughput, much lower heat transfer from the hot gas to the reactor walls would also be required so that the desired specific enthalpy be obtained before quenching. This appears entirely possible, for using the same argument used above for the anode, for the reactor shell, the heat transfer per unit throughput is expected to change as 1/D, for similar body temperatures. Thus 85% roughly drops to below 10% energy loss to the reactor body for a 10-fold increase in linear size.

Estimation of Minimum Energy Use for Larger Reactor

Unfortunately in practice the power dissipation which determines the electrical cost is not that dissipated at the anode, but that dissipated in the arc as a whole. The arc power is given by the product of the arc voltage and the current. The major part of the mass throughput (carbon) is uniquely related to

the current. The arc voltage is expected to remain roughly constant with increase in current (balance of increase with normal high current carbon arc and decrease with other arcs), perhaps at 70V. Thus to achieve a 25 kJ g^{-1} specific enthalpy of a carbon rich mixture from the arc, with no energy losses, a current I would have to be found which achieved a carbon ablation rate $\dot{m}_c(I)$ such that $70I/\dot{m}_c(I) = 25$ kJ g^{-1}. The projected performance of a reactor with a 33 mm diameter anode gives 70 x 1300 x 3600/5300 = 63 kJ g^{-1} for an anode feed velocity of 1.1 mm s^{-1} (c.f. the equivalent figure 240 kJ g^{-1} for the present reactor, a third of which is estimated to radiate - this radiation per unit throughput is assumed small for the large reactor). A higher current than 1300A, causing disproportionately greater ablation, would be needed to reduce this specific enthalpy further. The small reactor showed an increase of ablation of 1.5 g h^{-1} A^{-1} for increases of current, above 20A, with a calculated 86 to 78% waste of available energy at the anode. It was estimated above that this 'waste' would reduce to 8%, with an improvement of four times the energy utilization at the anode, for ten times the size of reactor. Thus an extrapolation above 1300A is used with a rate of increase in ablation of 1.5 x 4 = 6 g h^{-1} A^{-1}, giving $\dot{m}_c(I) = 5300 + 6(I-1300)$g h^{-1}. Using an arc voltage of 70V, the energy related to unit mass of carbon ablated is thus estimated to drop to 52 kJ g^{-1} at 2000A and 49 kJ g^{-1} at 3000A. A lower limit of about 50 kJ g^{-1} is thus expected from a scaled-up reactor of the type developed in this study, with a graphite

feed. With as much as a 90% conversion to acetylene, the minimum energy use for acetylene production is then expected to be about 14 kwh (kg acetylene)$^{-1}$, for a graphite anode ablating into hydrogen. Sufficient hydrogen to reduce the overall enthalpy to 15 kJ g^{-1} for a maximum conversion would result in mass C/H ratios of about 0.5 and acetylene concentrations of acetylene of only 2 to 3%. Clearly the graphite-hydrogen reaction would be unsuitable on this basis, the large energy use being the serious objection.

One way of avoiding this limitation would be to introduce additional carbon in the gas phase, perhaps by mixing the stream with methane. Assuming negligible heat transfer losses as above, and a 90% conversion, sufficient methane to bring the enthalpy of the combined stream to 15 kJ g^{-1} would result in mass C/H ratios of 4.0, with an energy requirement of only 5.5 kwh (kg acetylene)$^{-1}$ and an acetylene concentration from 25 to 30 mol %. The reactor would be then acting as an efficient heater of methane, and as a means of raising the acetylene concentration above that possible from methane-fed plasmatrons.

8.3 Coal Feed

Some progress towards providing a suitable coal feed was made by Dechasavapaisan (5) in a project related to this work. A steel tube filled with freshly pulverised coking coal was heated by radiation from a furnace at 1200K for several minutes. If the tube was sealed, at least for an initial period, rods of coke were formed which were porous, contained $\sim$ 25% of the original volatile matter of the coal ($\sim$35 mass %), and were thought sufficiently

strong and electrically conductive (only when heated to red heat) for use as anodes.

It is visualised that coal could be fed in pretreated rod form, or as a pretreated cylinder filled with untreated pulverised coal. In both cases, the anode would have to be porous to allow the gradual release of volatiles. A coking coal used to fill the cylinder would form an electrically conductive char, but may seal the escape of gaseous matter, perhaps blowing the anode apart. A non-coking coal is likely to be better in this respect, but would need to be graphitized before reaching the arc face. A mixture of coking and non-coking coals may prove to be the most practical solution. The coal char is likely to be much less dense and less homogeneous than the graphite used in this study. It is expected that the coal will be ablated more rapidly than the graphite, coming off the anode in larger fragments than those supposed from graphite.

Finkelnburg's experience (2) with anodes made from different sources of carbon may be useful here. Also many coals have appreciable quantities of ash, with sodium and potassium salts present. Thus the operation of a 'coal' anode may approach that for the anode of a Beck arc, which is loaded with metal salts. Finkelnburg found that what he called "soft core" carbons ablated more quickly than "hard core" carbons, and from his plots (2) it appears that for the same current, the ablation rate of the soft core carbons was double that for the hard core carbon. The anodes being used consisted of a cylinder of "hard" carbon filled by a core. This core could be

soft or hard, depending on whether the pulverised carbon used (lampblack, coke, graphite or a mixture) was made plastic before heating by mixing with tar or pitch, or was pressed with very little binder ("almost dry") into the shell. In both cases, the material was heat treated at 1500K before use. Baddour and Iwasyk (4) measured ablation rates in hydrogen with a graphite anode of the same diameter as the cored carbons used by Finkelnburg in one of his studies in air. The ablation rates of graphite in hydrogen were only a third of those with the hard core carbons in air. If the graphite is identified with the hard core carbons, in the same atmosphere, and an anode of coked coal identified with the pitch and carbon "soft core" carbons, then it would follow that ablation rates of twice that predicted for graphite would occur for the coked coal anodes.

This possibility would lower the energy dissipated in the arc for a given ablation. If all the assumptions made above for a large reactor using a graphite feed were assumed to hold for a coked coal feed, the specific enthalpy for ablated material could be dropped from 50 to 25 kJ g^{-1}. If this material could be held at this enthalpy for sufficient time to vaporise the particles, and then mixed with (more) hydrogen to produce acetylene with a conversion of 90%, the energy requirement would be only 7 kwh kg^{-1}. An addition of methane instead of hydrogen should reduce the energy consumption below this figure as estimated above.

8.4 Recommendations concerning electrode operation

In this study a busbar was used to connect the three cathodes together into the power supply. This presents an unstable situation if the arc falls with voltage as the current is increased, as the arc is likely to concentrate on one cathode to reduce its voltage. According to Finkelnburg, a carbon arc with a rapidly vaporising anode increases with voltage as the current increases. However, if one assumes a constant contact potential for his probe measurements, they show that all this increase in voltage occurs in front of the anode. If three cathode arc attachments are attempted well away from the anode, it is not likely that a rising voltage characteristic will hold for the section of arc which is open to choice - that is the three branches to the cathodes from the anode stream. To avoid the possibility of instability between cathodes, and so to allow control of conditions about each cathode tip, it is recommended that some separate ballast resistance be used in series with each cathode. An alternative which would involve rotation of the arc in a circle from cathode to cathode would be the supply of each phase of a three phase a.c. supply, after rectification, to one of the three cathodes.

It was not discovered in this study what the limitations of mass throughput with respect to stable arc operation were, as the device was limited by the current it was possible to pass to the anode, and from anode rod to anode rod. The design of the anode sliding contacts is regarded as crucial, for they must pass a high current to a rough surface, and operate at a

temperature probably above 1500K. The contacts between anode rods are even more difficult, as no significant pressure can be exerted between mating surfaces. If the anode was in the form of cylinders filled with coal, a coking coal could be used within the joint region to provide a solid coke mass to hold the joint before passing through the sliding contacts. If possible, a continuous manufacture of the anode would be the best solution.

8.5 Summary

In this chapter the requirements have been proposed for high concentrations and yields of acetylene from a reactor of the type in this study, and these are summarised in figure 8.2. It appears from the theory proposed in chapter 7 that vaporisation of carbon is not achieved completely at the anode of an electric arc and provision must be made to allow more complete vaporisation. With the higher gas phase C/H ratios resulting, high concentrations of acetylene should be possible from the "supercooling" theory, provided a temperature of about 1800 or 1900K is attained for a short time before the quench. Predictions were made concerning energy requirements in larger reactors. The effect of the reactor walls on the mass flow through the reactor is expected to diminish with size, making lower energy requirements per unit of acetylene possible, but with a graphite and hydrogen feed the projected energy use was still about 25% above a reasonable economic value (11 kwh kg^{-1}). Operation with methane was expected to bring the energy use down to 5.5 kwh kg^{-1}, well below the lowest plasmatron value for acetylene production with methane (9 kwh kg^{-1}).

Also operation with a coal or coked coal anode and hydrogen was expected to result in a lower energy use than that from operation with graphite and hydrogen, perhaps also lower than the plasmatron figure. The conclusion to be made here is that it appears worthwhile to pursue the development of this reactor to larger sizes.

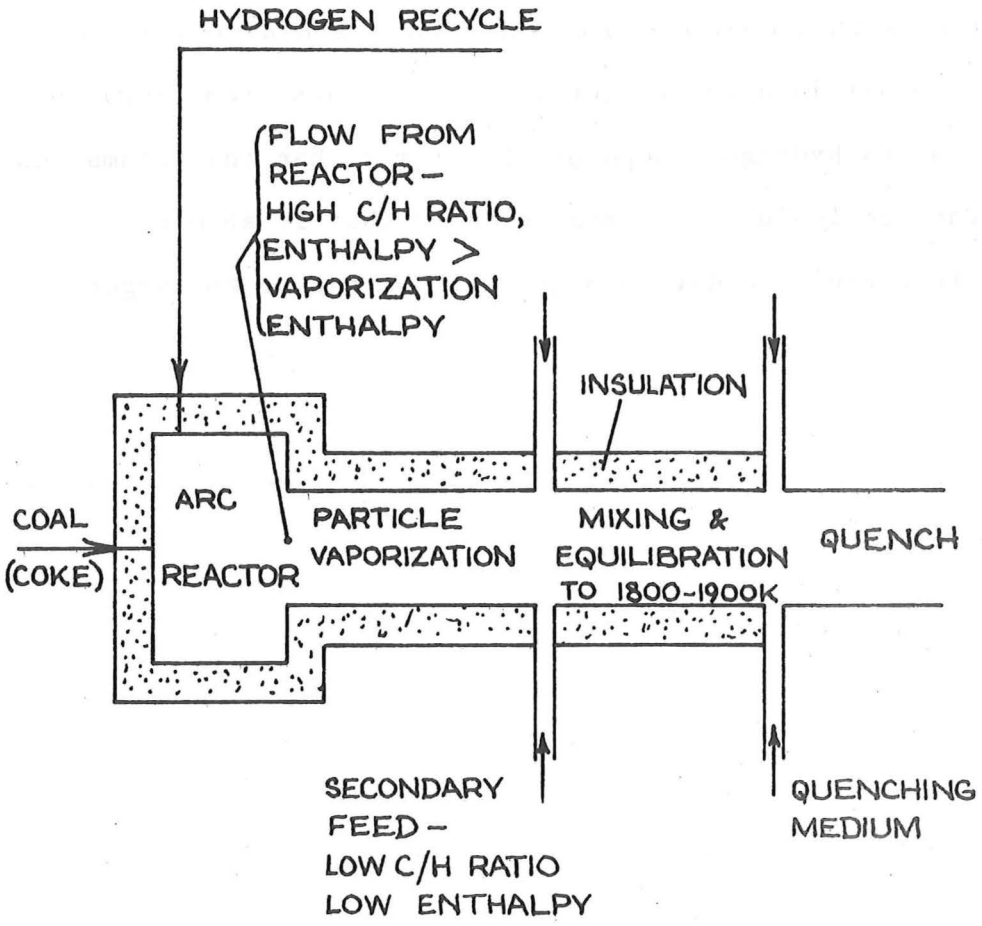


FIGURE 8.2 PROPOSED REACTION SCHEME

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APPENDIX 1.

N.Z. P.V.C. PRODUCTION PROPOSALS

New Zealand is probably spending over $10 million each year importing polyvinylchloride (p.v.c.) in bulk form to mould into plastic consumer items. In this paper the creation of a chemical industry in New Zealand to manufacture 40,000 tons of p.v.c./year has been considered. Two applicable processes with well-tried technology were costed in detail. The carbide process which uses coal, lime, and electricity to make acetylene from which p.v.c. can be made, is compared with the ethylene process which uses imported petroleum naphtha to make ethylene, from which p.v.c. can also be made. It is concluded that both processes give adequate return on capital after tax—the carbide process 18%/year and the ethylene process 21%/year for a capital expenditure of about $16 million in each case. It is also concluded that the carbide industry would be significantly more beneficial to the national economy, notwithstanding the lower profit to the investor. The developing technology for the use of natural gas and coal to manufacture acetylene at a significantly lower cost, is also discussed. It is suggested that natural gas can be regarded as an extremely valuable raw material for the manufacture of polymers. A coal-electric arc process, now under development at the Department of Chemical Engineering, University of Canterbury, promises much lower acetylene costs than the carbide costs.

Local coal, natural gas, or imported naphtha ?

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1. INTRODUCTION

THE polymers that are used today as plastics, rubbers, and fibres are mostly made up of hydrogen and carbon derived from petroleum, natural gas, or coal. These raw materials are chemically rearranged to form intermediate hydrocarbons, either acetylene or one of a group of olefins, from which polymers can be made. Acetylene has been a widely used chemical "building block" for manufacturing polymers for 20 years. The cheap production of the olefins, ethylene, propylene, and butadiene during the last decade, has severely challenged this role of acetylene in large industrialised nations.

When the relative merits of acetylene and olefin routes to polymers are compared for a small country like New Zealand, however, the economics of the use of acetylene become more attractive. Also acetylene can be made from local natural gas or coal, whereas ethylene or the other olefins can be made only from imported petroleum fractions. For these reasons some details of overseas production of acetylene are given.

1.1. Overseas experience with acetylene and ethylene

Acetylene has been manufactured on a commercial scale using calcium carbide for about 75 years. However, since the early 1950s increasing use has been made of petroleum and natural gas feed stocks for acetylene production[1], particularly by the BASF partial oxidation pyrolysis process.

To facilitate the use of liquid hydrocarbon feed stocks where ethylene is required as well as acetylene, processes have been developed which allow the heat to be supplied to the hydrocarbon from the previous burning of a fuel—e.g. the Hoechst process where a

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cheaper fuel than the feed stock hydrocarbon may be used. Both acetylene and ethylene can be formed by the pyrolysis of hydrocarbons in a preheated chamber —e.g. the Wulff process. Petroleum or natural gas feed stocks have also been pyrolysised in electric arcs to form acetylene. (The German plant at Huls produces 100,000 tons/year. Many attempts have been made to produce acetylene from hydrocarbons in a plasma jet.

Acetylene cannot be shipped easily or at low cost and cheap acetylene from calcium carbide is available only near a carbide plant which must be sited near coal and lime supplies. The hydrocarbon-based processes do not suffer this limitation, at least with a petroleum feed stock, because of the ease with which petroleum is transported.

A comparison of 1964 capital costs of plant[2] shows that for each annual million pounds of acetylene, $U.S.150,000 is spent for a 40 million lb/year carbide plant, and from $U.S.80,000 to $U.S.150,000 for hydrocarbon-based plants ranging within 25 to 100 million lb/year limits. In the United States average sales value of calcium carbide acetylene in 1965[3] was U.S.15.7c/lb. An acetylene selling price of U.S.13c/lb would be required to justify the construction of a new calcium carbide plant for 100 million lb/year of acetylene in the United States, and about 8c/lb of this would be direct costs (U.S. 0.60c/kWh)[3]. However, a new "average" hydrocarbon-based plant of 100 million lb/year capacity would require a selling price of U.S.8c/lb acetylene, with U.S.5c/lb of these in direct costs. The selling price quoted is the price required before it is economic to construct a new plant; the direct cost is the least that is required from the sales to avoid closing down existing plant.

It is significant that carbide plants in both the U.S. and Europe have been closed down in increasing numbers over the past decade. In the U.S. in 1953, production of acetylene from calcium carbide totalled about 436 million lb/year. This increased to about 707 million lb/year in 1960 but decreased to 610 million lb/year in 1965, and it is predicted, to 540 million lb/year in 1970. However, acetylene from hydrocarbons totalled 50 million lb/year in 1953 and by 1965 had risen to 550 million lb/year. Figure 1 shows production figures, where available[3, 4], for the three major users of acetylene in non-Communist countries —Japan produces almost all of its acetylene from coal, but this indicates a greater interest in ethylene rather than acetylene[5, 6]. Acetylene consumption in the U.S. in 1965[3] is listed in Table 1.

A choice between using acetylene or an olefin for production of a polymer can depend on the position of the investor. If all the plant, from raw material processing to production of the polymer, is to be new (as in New Zealand), the choice will be simply the route to the cheapest polymer. If the investor is financially committed to a less economic route, he is slow to change to a route made more attractive by an advance in technology. This commitment of many large European and American firms in plant using expensive acetylene has caused activity towards obtaining cheaper acetylene, rather than choosing to manufacture immediately with cheaper ethylene.

TABLE 1

Use of Acetylene in the U.S. in 1965

Outlet	*Percentage*
Vinyl chloride	27.5
Neoprene	21.0
Acrylonitrile	14.0
Trichloroethylene	9.0
Vinyl acetate	7.5
Other chemicals	8.0
Chemical subtotal	87.0
Non-chemical uses (welding, metal cutting, and carbon black)	13.0
Total (where 100% represents 1,150 million pounds)	100.0

A flow sheet of the present commercial routes from different feedstocks to the major monomers for which acetylene is a competitor is shown in Fig. 2. The numbers attached to the product boxes give the 1965 production in the U.S. by the indicated route, in millions of pounds of product.

The prominent competitor to acetylene is shown to be ethylene (Fig. 2). The large demand for ethylene in the manufacture of both polyethylene and polyvinylchloride (p.v.c.) has encouraged the building of enormous plants of 1,000 million lb/year of ethylene throughput. The economies of scale enjoyed by plants allow very low prices for ethylene. These large olefin plants produce a range of olefins from naphtha or gas condensate, and are distinguished from smaller ethylene plants optimised for yield of ethylene alone.

To challenge the price of ethylene of U.S.2.4c/lb obtained from very large plants, for the production of vinyl chloride and vinyl acetate, acetylene costs must come down to U.S.4c/lb and U.S.3c/lb respectively[3, 7, 8, 9]. This latter cost is claimed by one process only; one which has not yet reached industrial scale[18, 19, 20].

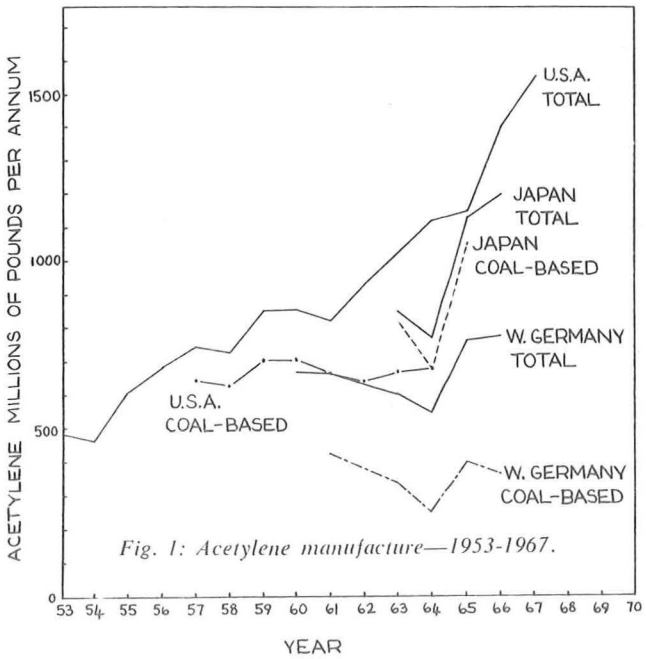
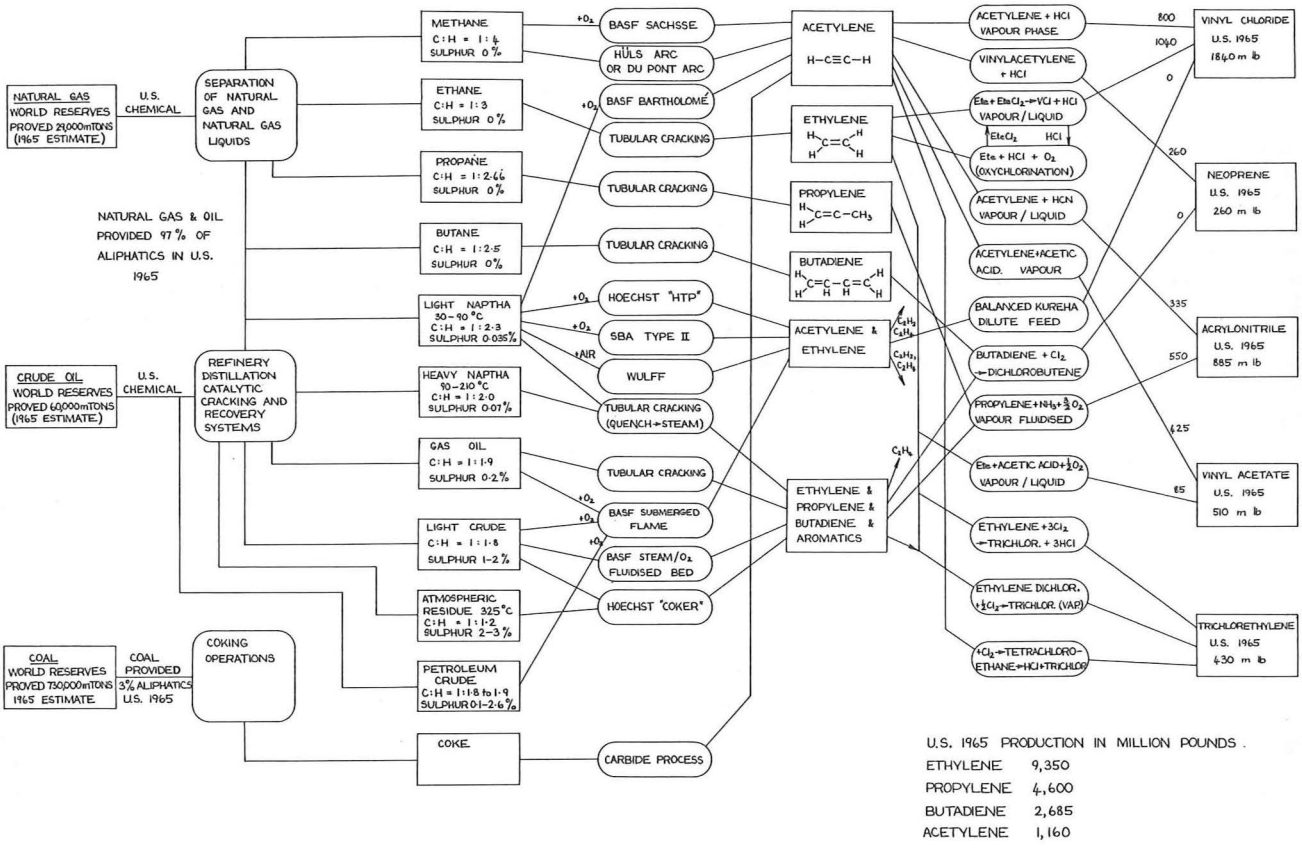


Fig. 1: Acetylene manufacture—1953-1967.

FIG.2 MAJOR ACETYLENE DERIVATIVES, FROM RAW MATERIALS WITH COMPETING ROUTES



2. NEW ZEALAND P.V.C. PRODUCTION

2.1. Reasons for domestic production

Interest is being shown in the production of plastics in New Zealand. There are several possibilities which are worth investigating for the supply of resins to the domestic market. The first possibility is p.v.c. because of the high volume of imports and the fact that the plant and experience for p.v.c. moulding is available in New Zealand. Other possibilities may be vinyl acetate (fibre), neoprene (rubber) and trichlorethylene (dry-cleaning solvent).

During the 1965-66 year, New Zealand imported 5,080 tons of bulk p.v.c. at a total cost of $N.Z.1,590,000 for manufacture of consumer articles[10]. The average imported cost was N.Z.14.0c/lb (U.S. 19.6c/lb). This corresponds to a post-devaluation price of N.Z.17.5c/lb. As imports of p.v.c. have been increasing rapidly since that time,and because many imported p.v.c. articles could be made in New Zealand if p.v.c. were less expensive, the present market potential can be safety set from 20,000 to 30,000 tons/year. It is estimated that domestic consumption would be greater than 40,000 ton/year of p.v.c. in the mid-1970s. This corresponds to at least $N.Z.13 million/year if imported. At this scale of production, p.v.c. could be manufactured in New Zealand cheaper than the imported cost of U.S.19.6c/lb. New Zealand would benefit appreciably from production of p.v.c. for the domestic market, particularly if the plant was New Zealand owned, and New Zealand raw materials were used.

2.2. Competition from overseas suppliers

It is likely that New Zealand production will be challenged by a drop in the import price of p.v.c. Any protection needed by the industry would best be estimated in advance and pressed for before production started. If no protection is needed, at least a good knowledge of the international supply and demand trends is necessary for the direction of a New Zealand industry.

In late 1967 it was estimated that global capacity of p.v.c. plant was 5 million tons/year with consumption of 3.5 million tons, and a consequent apparent 70% utilisation of plant[11]. After allowing for the tendency of some producers to give too high values of production capability of their plant by from 10 to 20%[12, 13], the surplus of p.v.c. was still significant. As a result, overproducing countries dumped p.v.c. in those countries where costs were greater. It was reported[11] in 1967 that Japan was selling p.v.c in Britain for as low as U.S.9.3c/lb for some grades, undercutting United Kingdom prices of U.S.12 to U.S.13c/lb. Against such pressure on New Zealand production of p.v.c., the New Zealand Government

could perhaps set up protective tariffs as the Australian Government did in 1966 to protect Australia's plastic industry which had a $A.250 million capital investment.. As well as normal tariffs, special punitive duties against dumping were imposed[14], effectively placing a lower limit of A.18.3c/lb (U.S.20.5c/lb) on p.v.c. and A.16.7c/lb (U.S. 18.7c/lb) on imports of vinyl acetate monomer.

Since 1967 the international market for p.v.c. has lost most of its surplus supply. At the end of 1968, demand and production of p.v.c. were in balance in both the European Economic Community (E.E.C.) countries and the U.K.[13]. Price increases of 5 to 15% were announced by producers in the E.E.C. In the U.S., supply and demand of p.v.c. balanced in mid-1969[12], causing a stop to the downward trend of p.v.c. prices. A 20% increase of p.v.c. production rate during 1969 was forecast in Europe, whereas a smaller increase of 13% was likely in the U.S. Producers seem confident that prices of p.v.c. in Europe will not drop despite the strong increase in production.

2.3. Raw materials

The raw materials needed for p.v.c. production include raw materials for the hydrocarbon intermediate—acetylene or ethylene—and salt in some form suitable for making chlorine and hydrogen in an alkali-chlorine cell. If acetylene is used as the intermediate, coal and lime, natural gas or petroleum naphtha can be chosen as raw materials. If ethylene is used, one is restricted to imported naphtha. New Zealand has large resources of coal of suitable quality, some natural gas, but little discovered oil. If oil was discovered it seems doubtful whether a naphtha stream could be separated from the crude oil at anywhere near the low cost of 1c/lb, for which it is available in the Pacific area. Even at this cost, a p.v.c. production of 40,000 tons/year would cost the country N.Z.1.7c/lb p.v.c.—i.e., $N.Z.1,500,000/year for imported naphtha. In view of the expansion of a New Zealand industry, and the steady rise of naphtha prices overseas, it would be wise to use New Zealand raw materials if the process costs are at all comparable.

2.4. Process costs in small plants

Much of the cost advantage that ethylene has in large markets overseas is due to the enormous size of plants producing ethylene. Plants capable of producing 500,000 tons/year of ethylene are found in the U.S., Europe, and Japan. Much of this advantage is lost when much smaller plants are considered. However, a simplified ethylene plant, stripped of many cost-saving features found in large plants, has been designed for low-production rates. Costs of production of vinyl chloride monomer from ethylene or acetylene were compared in 1967 for small plants of only 12,700

TABLE 2

Vinyl chloride monomer plants
Production and Capital Costs for 12,700 tons/year

Figures in U.S.c/lb *Item*	*Dianor dilute ethylene* Naphtha feed	*Wulff acetylene* Naphtha feed	*Carbide acetylene* Carbide feed	*Ethylene from ethanol* Ethanol feed	*Kureha mixed feed* Naphtha feed
Ethylene/Acetylene production					
Net feedstock cost	1.87 (3.07)*	3.31	21.40 (15.4)†	5.50	
Utilities	0.14	0.53	0.02	0.80	See
Labour and supervision	0.14	0.14	0.14	0.14	below
Maintenance, depreciation, taxes, overheads	2.12	5.14	1.78	2.00	
Total hydrocarbon cost (return on capital not included)	4.3 (5.5)*	9.91	23.3 (17.3)†	8.05	
Vinyl chloride monomer production					*(Total process)*
Net feedstock cost	3.80 (5.63)*	4.91	11.01 (8.3)†	5.80	3.10
Utilities	0.86	0.20	0.20	0.86	1.90
Labour and supervision	0.05	0.05	0.05	0.05	0.40
Maintenance, depreciation, taxes, overheads	1.24	0.99	0.99	1.24	2.50
Vinyl chloride manufacturing cost	5.95 (7.78)*	6.15	12.25	7.95	7.90
20% return on total investment	2.70	3.74	2.02	2.60	2.90
Vinyl chloride transfer price—total cost	8.65 (10.48)*	9.89	14.27 (11.0)†	10.55	10.80
Capital costs (figures in $U.S. million)					
Hydrocarbon plant	1.2	2.5	0.85**	1.13	2.8
Vinyl chloride plant	1.4	1.1	1.1	1.4	
Offsite and working capital	0.9	1.6	0.85	1.07	1.2
Total	3.7	5.2	2.8**	3.6	4.0

* The figures in brackets have been corrected for yield of ethylene from naphtha, and for a higher chlorine cost, more appropriate to New Zealand. For the Dianor process, a weight yield of acetylene of 50%, and a naphtha cost of U.S.0.95c/lb appears to have been assumed. The latter price is optimistic, as it is the price of big shipments in Europe. Considering the maximum yield of ethylene from a tubular cracking furnace before severe coking occurs[16], and allowing for recycle of propylene, no more than 31% weight yield ethylene can be made. A chlorine by-product stream costed at U.S.1.4c/lb, from caustic soda manufacture, has been assumed. A full production cost of U.S.2.4c/lb will have to be used for New Zealand conditions. The original table seems to have been hastily made, for a considerable under-estimation for 20% return on investment for the Kureha process was found.

**The carbide is imported. Cost of a carbide plant is not included.

† For these figures lower power costs were charged to the carbide, as would be appropriate if it were made in New Zealand. A unit cost of N.Z.0.4c/kWh (U.S. 48c/kWh) replaced U.S.1.8c/kWh assumed in the carbide production.

tons/year[15], including the small Dianor "drawing board" ethylene plant. Battery limits investment costs were raised 45% to allow for off-sites and working capital. This figure is suitable for less developed countries than New Zealand, but for New Zealand 25% would be a more realistic allowance. Utilities were costed at "values normally prevailing in the less developed countries". The breakdown of production and capital costs for linked acetylene/ethylene units and vinyl monomer plants is given in Table 2.

The Wulff process uses a high temperature cyclic cracker to pyrolyse naphtha to acetylene. The Kureha process produces balanced streams of ethylene and acetylene from naphtha, completely utilising the chlorine supply. This has been a problem with ethylene plants until the introduction of oxychlorination in 1964, which is economic for larger plants. For the sale of p.v.c., a polymerisation step must be added to the above scheme. From a report[17] of details of a new French bulk p.v.c. polymerisation process, high-grade p.v.c. can be produced from vinyl chloride for U.S.1.4 c/lb p.v.c. in a 30,000 tons/year plant. If polymerisation costs were reckoned at U.S.2.0c/lb in New Zealand for a production of 12,700 tons/year, the p.v.c. selling price would be lowest for the Wulff process at U.S.11.9c/lb and highest for the carbide process at U.S.13.5c/lb. As these costings already include a 20% return on capital and are 31 to 39% below the current import price of p.v.c., production in New Zealand may be commercially viable even for a small 13,000 tons/year plant.

2.5. Process costs for larger plant—naphtha ethylene and carbide acetylene

Since demand of p.v.c. at present may be as high as 30,000 tons/year, plants of 20,000 to 40,000 tons/year will now be considered. The Wulff and Hoechst processes should be considered possibilities, but the comparison here will be restricted to the carbide process, which uses New Zealand raw materials, and the ethylene processes which are probably the cheapest processes of those fed with imported naphtha. A more complete costing analysis is shown in Table 3 for the Dianor dilute ethylene process, a conventional oxychlorination ethylene process, and in Table 4 for the carbide process. The costs of major items are: naphtha —N.Z.0.8c/lb; coal—$N.Z.6.0/long ton; lime—$N.Z. 7.0/long ton; electricity—N.Z.0.4c/kWh.

In Tables 3, 4, 5, 6, the p.v.c. process costs do not include any return on capital borrowed. To this extent, they cannot be compared with those costs arrived at for p.v.c. from Table 2. Instead, the profit is calculated as

TABLE 3

Production costs for 20,000 and 40,000 tons/year p.v.c. manufacture in New Zealand using the Dianor and oxychlorination processes[15, 18]

(figures in N.Z. currency)

Production. long tons/year	20,000		40,000	
Process	Dianor	Oxychlorination	Dianor	Oxychlorination
Ethylene production costs c/lb				
Naphtha at 0.8c/lb, 3.2 lb	2.58	2.53	2.58	2.58
Utilities	0.12	0.67	0.12	0.67
Labour and supervision	0.12	0.05	0.12	0.05
Plant general expense	0.08	0.03	0.08	0.03
Maintenance, depreciation, taxes, overheads at 25.5% plant cost*	1.52	2.84	1.15	2.22
Total ethylene process costs	4.42	6.17	4.05	5.65
Vinyl chloride costs c/lb				
0.5 lb ethylene	2.21	3.08	2.02	2.82
1.2 lb (0.6 lb)chlorine at 2.0c/lb	2.40	1.20	2.40	1.20
Utilities	0.67	0.22	0.67	0.22
Labour and suprevision	0.04	0.06	0.04	0.06
Plant general expense	0.03	0.04	0.03	0.04
Maintenance, depreciation, taxes, overheads at 25.5% plant cost	0.90	1.47	0.67	1.15
Total vinyl chloride costs	6.25	6.07	5.83	5.49
P.V.C. production costs c/lb				
1.03 lb vinyl chloride	6.43	6.25	6.00	5.65
Initiators	0.16	0.16	0.16	0.16
0.08kWh at 0.4c/kWh	0.03	0.03	0.03	0.03
Labour and supervision	0.40	0.40	0.30	0.30
Plant general expense	0.30	0.30	0.20	0.20
Maintenance, depreciation, taxes, insurance at 25.5% plant cost	0.79	0.79	0.61	0.61
P.V.C. process costs c/lb	8.1	7.9	7.3	7.0

* This item was built up using the assumptions: Maintenance, 5.0%; insurance, 0.5%; property tax, 1.0%; overheads, 10.0%; depreciation, 9.0%; Total, 25.5% plant cost.

TABLE 4

Production costs for 20,000 and DJ,JJD *tons/year*
Production costs for BB,BBB *and 40,000 tons/year*
p.v.c. manufacture in New Zealand using the carbide process

(figures in N.Z. currency)

	20,000	40,000
P.V.C. production, tons/year		
Coke production costs $/ton		
1.43 tons coal at $6/ton	8.6	8.6
Firebars	1.0	1.0
Labour	0.2	0.1
Maintenance, depreciation, taxes, insurance at 25.5% capital	2.0	1.4
Credit for 500 kWh/ton	(2.0)	(2.0)
Total production cost	$9.8	$9.1
Calcium carbide production costs $/ton		
0.98 tons of lime at $7/ton	6.9	6.9
0.65 tons coke	6.4	5.9
Electrode carbon at 4.5c/lb	2.0	2.0
Miscellaneous chemical supplies	0.4	0.4
Total materials	15.7	15.2
3,400 kWh at 0.4c/kWh	13.6	13.6
Labour (3 manhours at $1/h.)	3.0	3.0
Plant general expenses	2.4	2.4
Insurance, taxes and depreciation at 25.5% capital	21.7	16.6
Total production cost of carbide/ton	$56.4	$50.8
Acetylene costs c/lb		
3.6 lb carbide	9.1	8.2
Utilities	0.02	0.02
Labour	0.1	0.05
Maintenance, depreciation, taxes, insurance at 25.5% capital	0.66	0.53
Total process costs c/lb	9.9	8.8
Hydrogen chloride production costs c/lb		
Chlorine cost $47/ton from $8/ton Australian salt using mercury cell (with hydrogen)	2.1	2.1
Maintenance, depreciation, taxes, insurance at 25.5% capital	0.20	0.15
Hydrogen chloride process costs c/lb	2.3	2.3
Vinyl chloride production costs c/lb		
0.43 lb acetylene	4.3	3.8
0.59 lb chlorine	1.3	1.3
Catalysts and chemicals	0.3	0.3
Total materials cost	5.9	5.4
0.10 kWh at 0.4c/kWh	0.04	0.04
Steam and cooling water	0.1	0.1
Labour plus supervision	0.09	0.07
Plant general expense	0.06	0.05
Maintenance, depreciation. taxes, insurance at 25.5% capital	1.10	0.85
Total vinyl chloride process costs	7.3	6.5
P.V.C. production costs c/lb		
1.03 lb vinyl chloride	7.5	6.7
As for ethylene route	1.7	1.3
P.V.C. process costs c/lb	9.2	8.0

an annual return on all fixed capital after income tax has been levied. Profit is shown as a function of the p.v.c. selling price in Fig. 3 for the three processes, and for production of 20,000 and 40,000 long tons/year. An example of the working is shown in Table 6 where the p.v.c. is sold for N.Z.14.0c/lb, the 1965 imported price. The post-devaluation imported price is likely to be N.Z.17.5c/lb. The carbide process has the penalty of slightly higher capital cost, largely owing to the carbide furnace, and the penalty of higher raw materials costs, with the result that the oxychlorination of ethylene is more profitable to the investor. In the estimation of plant capital, the following formula was used to convert cost of plant for some quoted production rate, to that for the desired production rate—i.e.

$$C_1 = C_0 \, r^{0.6}$$

where C_0 = quoted cost
C_1 = desired cost
r = ratio of desired throughput to quoted throughput.

An error of ± 10% should be allowed for individual items of plant for this procedure. The production costing should be more accurate than this, so that it can be said confidently that the profitability of the ethylene processes is greater than that of the carbide process.

2.6. A national viewpoint

It is interesting to look at Table 6 from the point of view of the New Zealand economy as a whole. For 40,000 tons/year of p.v.c. production the cost to the State of the carbide route as compared with the oxychlorination of ethylene, can be estimated.

Table 7 shows that from a national standpoint, the cost of manufacture of 40,000 tons/year of p.v.c. by the ethylene route from imported naphtha is 50% more than the cost by the carbide route.

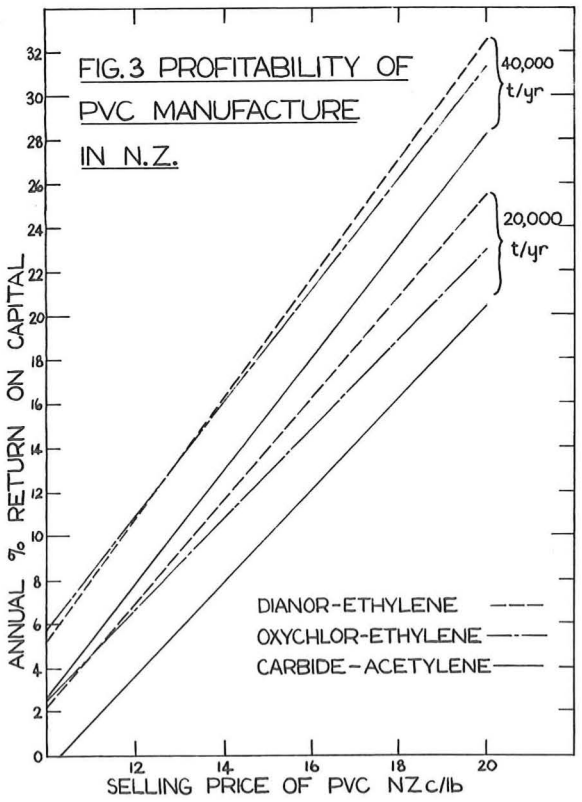


TABLE 5

Capital costs of plant for manufacture of p.v.c. in New Zealand (figures in $N.Z. million)

Process		*20,000 tons p.v.c./year*					
		Dianor		*Oxychlorination*		*Carbide*	
		tons/year	*$m*	*tons/year*	*$m*	*tons/year*	*$m*
Plant	*Product*						
Coker	Coke					17,000	0.13
Carbide furnace	Carbide	23,600	2,62	11,800	1.30	28,300	2.42
Alkali-chlorine cell	Cl_2,H_2,					12,100	1.30
Chlorine burner	HCl	10,000	1.33	10,000	2.50	12,100	0.22
Hydrocarbon plant	C_2H_2,	20,000	1.54	20,000	2.60	8,600	0.53
Vinyl chloride plant	C_2H_4	20,000	1.39	20,000	1.39	20,000	1.93
Polymeriser	C_2H_3Cl					20,000	1.39
Total plant capital cost $M	P.V.C.		6.88		7.79		7.62

Process		*40,000 tons p.v.c./year*					
		Dianor		*Oxychlorination*		*Carbide*	
		tons/year	*$m*	*tons/year*	*$m*	*tons/year*	*$m*
Plant	*Product*						
Coker	Coke					34,000	0.20
Carbide furnace	Carbide	47,200	5.24	23,600	2.62	56,600	3.66
Alkali-chlorine cell	Cl_2,H_2,					24,200	2.62
Chlorine burner	HCl	20,000	2.00	20,000	3.70	24,200	0.34
Hydrocarbon plant	C_2H_2,	40,000	2.30	40,000	4.05	17,200	0.80
Vinyl chloride plant	C_2H_4	40,000	2.12	40,000	2.12	40,000	2.94
Polymeriser	C_2H_3Cl					40,000	2.12
Total plant capital cost $M	P.V.C.		11.66		12.49		12.68

TABLE 6

Profitability of p.v.c. manufacture in New Zealand—selling price N.Z.14.0c/lb (figures in $N.Z. million)

	20,000 tons/year			*40,000 tons/year*		
	Dianor	*Oxychlor-ination*	*Carbide*	*Dianor*	*Oxychlor-ination*	*Carbide*
Sales turnover	6.25	6.25	6.25	12.50	12.50	12.50
Production cost	3.63	3.53	4.11	6.54	6.27	7.15
	2.62	2.72	2.14	5.96	6.23	5.35
Administration, 10% sales	0.63	0.63	0.63	1.25	1.25	1.25
Net profit before tax	1.99	2.09	1.51	4.71	4.98	4.10
Tax at 50%	0.99	1.04	0.75	2.35	2.49	2.05
Net profit after tax	0.99	1.04	0.75	2.35	2.49	2.05
Plant fixed capital	6.88	7.79	7.62	11.66	12.49	12.68
Associated capital 25%	1.72	1.95	1.90	2.90	3.13	3.17
Total capital	8.60	9.74	9.52	14.56	15.62	15.85
Return on capital after tax	11.5%	10.7%	7.9%	16.1%	16.0%	13.0%

From Tables 3-7 and Fig. 3, several points emerge:

(1) It is likely that a price of N.Z.16c/lb for p.v.c. would compete with present import prices. Assuming this selling price, and that a capital return of 15%/year is required before a process is considered economic, then both ethylene processes are economic for a 20,000 tons/year plant, whereas a carbide plant must produce 30,000 tons/year before it is economic.

(2) The ethylene processes are more profitable than the carbide process by 3 to 3½% return of capital. The Dianor process has a definite advantage in profit over the oxychlorination process for 20,000 tons/year throughput, but the advantage is not significant at 40,000 tons/year.

(3) In contrast to the above, manufacturing p.v.c. through the carbide route costs considerably less in foreign exchange to New Zealand than using an ethylene process.

2.7. Summary of p.v.c. costs

The coker considered is a continuous, automatically-controlled travelling-grate coker, similar to the 13,000 tons/year coker that Shawinigan Chemicals Corporation in Toronto use to supply a carbide plant. Since the coking rate is about 50 lb/ft²h compared with 2.3 lb/ft²h for dry distillation cokers, the investment costs are reduced tenfold. According to Baum[19] the offgases can be used to generate from 325 to 860 kWh/ton coke produced, if use is made of the sensible heat and heating value of the reaction gases to raise steam.

TABLE 7

National economic comparison between the carbide process and the ethylene oxychlorination process for 40,000 tons/year of p.v.c.

Ethylene oxychlorination process overseas expense

Item	*$NZ/year*
9% interest on plant fixed capital	1,120,000
66,000 tons naphtha at $18/ton	1,190,000
Total	2,310,000

Carbide process overseas expense

Item	*$NZ/year*
9% interest on plant fixed capital	1,140,000
7% interest on overseas capital for electric power ($130/kWh—i.e. ⅓ N.Z. outlay)	250,000
Electrode carbon (100% overseas content)	114,000
Firebars for coker (100% overseas content)	34,000
Coal (assume 10% overseas content)	15,000
Lime (assume 10% overseas content)	20,000
Total	1,573,000
Extra expense involved in using naphtha. $/year	$737,000

The carbide furnace would best be a modern, hollow, electrode furnace which will accept up to 20% of fine material in the feed[20]. Acetylene and ethylene plants with their vinyl chloride plants are a standard type of plant[18, 21].

To provide a chlorine supply. an alkali-chlorine electrolytic cell fed with a concentrated sodium chloride brine was assumed. Lake Grassmere salt works could not supply the required tonnage, so Australian salt would have to be imported at $N.Z.8/ton. If this supply of salt was used, a mercury cell would be more desirable than its alternative, a diaphragm cell, since a high-purity caustic-soda by-product could be sold to soap manufacturers. However, a diaphragm cell can be fed with a brine of 15% salt by weight as this brine is concentrated to the 28% by weight concentration needed for cell operation by addition of salt obtained from the outgoing liquors. An electrodialysis unit, as supplied by Japanese manufacturers, can supply a salt-water brine of 15% weight salt from sea water (less than 3% by weight of salt) for $N.Z.8/ton salt[22], costed under Japanese conditions. A diaphragm cell may prove more economic with such a supply. Alternatively, if cheap steam was available in the plant, it could cost no more than $1/ton to evaporate 15% brine to a saturated 28% brine suitable for a mercury cell. These possibilities should be investigated.

3. NEW CHEAPER METHODS OF ACETYLENE MANUFACTURE FROM NATURAL GAS AND COAL

From the cost analysis in sections 2.5-8, p.v.c. could be manufactured at a price acceptable for domestic consumption. To give New Zealand manufacturers of p.v.c. goods some start in the export market, cheaper p.v.c. would be needed. At the scale of New Zealand production, this requires a process with relatively small capital investment. The only step which appears amenable to change is the manufacture of the hydrocarbon intermediate with perhaps simplification in the vinyl chloride plant according to the composition of gases from the hydrocarbon plant. The ethylene route appears not accessible to radical technical advances[16], whereas several possibilities exist with the manufacture of acetylene. A one-step process with high throughput and little gas separation plant would be ideal.

3.1. Natural gas

Othmer, Happel and Kramer used electrically-heated tubes to pyrolyse natural gas to acetylene in a pilot plant in the United States [23]. They report[24] methane conversions to acetylene of over 96% of theoretical, with a product gas composition of 21% acetylene, 5% methane and the rest hydrogen. The pyrolysis plant with separation facilities included is estimated to have a capital cost of U.S.5 to 8c/lb yearly capacity of acetylene. This compares well with the carbide process capital cost of U.S.13.6c/lb acetylene capacity at 17,000 tons/year size. Othmer claims that if natural gas is costed at 20c/1000 ft^3, and the hydrogen can be sold for 30c/1000 ft^3, acetylene can be produced for only 3c/lb. If the hydrogen is used as fuel, the acetylene cost is claimed to be 5c/lb. Patents were taken out in 1965[25], but no full-scale plant is known to the authors.

If this process is as attractive as it appears, New Zealand would do well to consider any natural gas which is found as a valuable feedstock for plastics manufacture. In May 1967, the New Zealand Government reached an agreement with Shell-B.P.-Todd Oil Services[26] to receive natural gas at the Kapuni wellhead for N.Z.21d (N.Z.17.5c)/therm (100 ft^3 of methane). Costs of removing a large fraction of carbon dioxide would be added to this, and interest on the $18,000,000 capital cost of the carbon-dioxide treatment plant and compressor station alone amount to about 9c/1000 ft^3 for the entire field. Taking the optimistic value of N.Z.30 to 35c/1000 ft^3 of methane as an approximate c osting of the natural gas at Kapuni, the Othmer process would produce acetylene at almost one cent dearer than the patentor's claim in the U.S. Very approximately, acetylene could be produced for 6c/lb from Kapuni gas. The estimated reserves of Kapuni natural gas are reported[27] as being the thermal equivalent of 0.63 million tons of coal. This represents 0.35 million tons of methane. If 0.1 million tons of this was available for chemical manufacture, with 70% yield, 160,000 tons of p.v.c. would be produced. If an average of 40,000 tons of p.v.c. was needed in New Zealand over the next 10 years, only four years of feedstock would be available. At this rate, investment in plant would not be economic. However, oil prospectors apear to have found a larger gas field off the Taranaki coast. The possibility of a polymer industry based on this gas should be thoroughly investigated.

3.2. Coal

New Zealand has large reserves of coal with relatively low ash content, and with a low cost of mining compared with many parts of the world. A fresh look into the utilisation of coal as a raw material has been made by the authors. Promise has been shown by electric arc devices, by their achieving economic and near-economic yields of acetylene. Graphite requires about half the energy to convert with hydrogen to acetylene, as it takes to convert methane to acetylene. Coal can be said to be roughly similar to graphite in this respect. Thus the minimum power usage possible with a methane-rich natural gas is 4.36 kWh/kg C_2H_2, compared with the minimum with coal of 2.4 kWh/kg C_2H_2. A significant advantage in energy costs should be achieved by using coal. The possibility remains

that coal could be vaporised in an arc device, utilising fully the hydrogen and carbon of coal for acetylene synthesis. Such an arc device would have to be designed specifically for a coal feed with the aim to optimise on energy usage and once-through yield. An experimental project on these lines was begun in 1966 in the Department of Chemical Engineering, University of Canterbury on a small scale.

The reactor operates at 1 to 4 kW and was designed for a maximum throughput of 1 lb/h, with a working volume of about one twentieth of that for the Othmer process with the same throughput. Mechanical feasibility, a non-trivial problem for components surrounding an arc, has been largely solved, and acetylene yields have been very promising. At most, the possibility of economic feasibility of such a process can be shown here to justify the technical programme being carried out.

From a 1966 estimate of the cost of mining of coal in New Zealand[28], pithead cost was N.Z.0.27c/lb. Hydroelectricity costs from N.Z.0.274c/kWh (Manapouri) to produce without transmission costs, according to the 1967 White Paper[29]. If electricity was generated near the chemical plant from coal—all situated at a coal mine—coal costs alone for one kilowatt-hour assuming an efficiency of 36% are N.Z.0.27c. If one assumes a total generation cost of 0.4c/kWh and a power usage of 5.6 kWh/lb acetylene (including purification) as obtained with the Du Pont and Huls arc reactors, power costs would amount to N.Z.2.24c/lb acetylene. If one also assumed a yield of 35% by weight as with the Huls plant (the Du Pont yield is higher), feedstock costs would amount to N.Z.0.77c/lb acetylene. It is estimated[30] that the cost of production of acetylene in the Du Pont acetylene plant over and above the cost of raw material and power in a 25,000 tons/year plant ($U.S.7.2M), amounts to U.S.3.3c/lb. The total cost of acetylene from such a hypothetical arc reactor using coal is shown in Table 8.

TABLE 8

Acetylene costs from a New Zealand coal-fed arc process

Item	*Costs/acetylene*	
Power	N.Z.2.24c	(U.S.2.50c)
Coal	N.Z.0.77c	(U.S.0.86c)
Utilities, labour, maintenance, overheads, depreciation, plus interest (latter at 15%)	N.Z.2.9c	(U.S.3.3c)
	N.Z.5.9c	(U.S.6.4c)

(c.f. N.Z.11c/lb for carbide acetylene in New Zealand)

Hopefully, the capital cost of such a reactor would be smaller than the large cost of the Du Pont reactor quoted above, and further economies on power usage and yield could be made. This acetylene cost is equivalent to an ethylene cost of N.Z.4c/lb, and so is well below the cost of any other possibility in New Zealand except the Othmer process. Some hydrogen may be needed in the above process, adding perhaps 0.5c to the above cost.

It is significant that the Office of Coal Research in the U.S. Bureau of Mines made a $2,000,000 contract with A.V.C.O. Space Research Centre, Massachusetts, in 1967 to investigate the possibility of obtaining acetylene cheaply from coal in an electric arc reactor[31]. The basic idea behind their design was the same as that used by the authors in building their reactor. A.V.C.O. have spent $800,000 since 1967, and have attempted three designs of 100 kW rating to achieve mechanical feasibility. In their third reactor they have achieved a 25% by weight yield of acetylene from coal, with a 9% by volume concentration of acetylene in the off-gases, and a power demand of 5.5 kWh/lb acetylene, presumably in the arc alone. Hypothetical plant designs for both 150 and 300 million pounds of acetylene per year plants have been worked out by Stone and Webster Engineering Corporation, and indicate that acetylene would cost U.S.7 to 8c/lb to produce, allowing for a 12% return on capital, and taking the cost of electricity as U.S.0.525c/kWh. The cost of plant is not divulged.

The basic idea is the efficient use of the electrical energy in the arc to vaporise a consumable solid coal anode. Owing to mechanical difficulties encountered by A.V.C.O. workers in the area surrounding the anode, they at present use a strong flow of hydrogen to give a partially fluidised feed of coal through the anode region, together with a magnetically-spun arc to increase the contact between coal and arc. This represents a practical compromise with the original idea, which has lost, in the authors' opinion, much of the possible advantage of the arc configuration used. However, A.V.C.O. workers are reported optimistic about lowering the acetylene cost further. The study made by Stone and Webster indicates that a power usage of as little as 3.5 to 4 kWh/lb acetylene must be achieved if the process is to become viable in the U.S. The A.V.C.O. group plan to build a one megawatt 10 tons/day pilot plant in the near future.

With the development of processes such as the Othmer process, and the coal-arc processes, New Zealand natural gas and coal could be valuable chemical raw materials. The coal-arc process is envisaged as using both coal and natural gas, where economic. Air pollution problems from such a plant would be non-existent, for any sulphur present in the coal would be completely broken down to either hydrogen sulphide or sulphur dioxide, which are easily removed. Any nitrogen present would be reacted to give hydrogen cyanide, which is itself a valuable starting material for chemicals. Direct reaction between hydrogen cyanide and acetylene yields acrylonitrile. If this could be arranged in the dilute product gas itself, a one-step process from coal, nitrogen and perhaps natural gas, to acrylonitrile would have been achieved. With a vast preponderance of coal in the remaining hydrogen and carbon bearing deposits in the world, and the coming of cheaper power from nuclear reactors, it will eventually become an economic necessity to use more drastic methods of rearranging carbon and hydrogen to suit the needs of tomorrow's society. The milder ethylene route to polymers relies on the more convenient chemical and physical arrangement of petroleum, which is expected to be running short in the 1980s or 1990s[32].

4. CONCLUSIONS

(1) A case has been made for p.v.c. manufacture in New Zealand. The present use of imported p.v.c. may be as high as 30,000 tons/year, which would cost

the country over $8 million/year in overseas exchange.

(2) Production and capital costs were estimated for Dianor ethylene, conventional ethylene oxychlorination and carbide acetylene based plants for manufacturing p.v.c. at the rates of 20,000 and 40,000 tons/year. Profitability in terms of annual return on capital after tax was also calculated. The ethylene processes yield 3 to 3½% capital more does the carbide process. The ethylene processes need to be only 20,000 tons/year in capacity to yield 15% return on capital when the selling price of p.v.c. is N.Z.16c/lb. By comparison, the carbide process needs to be 30,000 tons/year in capacity for the same profitability.

(3) From the national economy viewpoint, the carbide process, using New Zealand raw materials, is cheaper by $700,000/year than the oxychlorination of ethylene, for a production of 40,000 tons/year of p.v.c. This production would cost New Zealand $1,600,000/year in overseas exchange using the carbide route.

(4) In planning technical development in future years for production of polymers in New Zealand, the use of natural gas and coal is urged. The only possibility for these raw materials is the manufacture of acetylene from them. Two processes, both of which use electric power, are discussed. One, for natural gas, is at least at the pilot-plant stage in the U.S., and would be a very valuable possibility for the Maui gas field. The second process is under development at both the Department of Chemical Engineering, University of Canterbury, and at the A.V.C.O. Corporation in the United States. This process converts coal directly to acetylene through an electric arc. The American effort has shown commercial feasibility and is almost at the pilot-plant stage, whereas the effort at Canterbury shows promise at a small scale. The authors urge the further support of this effort.

5. ACKNOWLEDGMENTS

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APPENDIX 2

DESIGN INFORMATION

Thermodynamic data from JANAF tables (reference 3.3):

Enthalpy of formation of methane $\Delta H^{o}_{f298} = -75.0$ kJ mol^{-1}

Molar enthalpy of acetylene $H^{o}_{2000} = 338.0$ kJ mol^{-1} w.r.t. H_2, C_s, 298K

Molar enthalpy of hydrogen $H^{o}_{2000} = 53.0$ kJ mol^{-1} "

Enthalpy of sublimation of carbon (calculated from equilibrium composition of C, C_2, C_3, C_4 and C_5 at 4100K, and using JANAF data for these species and graphite)

$\Delta H_{sublimation} = 280$ kJ mol^{-1} carbon

Molar enthalpy of graphite $H_{4100K} = 55$ kJ mol^{-1}

APPENDIX 3

SPECTROSCOPIC QUANTITIES

Radiance of the Low Current Graphite Arc

(from reference 6-2)

Wavelength/nm	Radiance/W cm^{-3} sr^{-1}
365	61.1×10^4
395	92.3 "
430	123 "
480	175 "
525	220 "

Oscillator Strength - Degeneracy Products for the Balmer Electronic Transitions of the Hydrogen Atom

(from reference 6-6)

Line	Wavelength/nm	gf	Relative E/cm^{-1}
H_β	486.1	0.955	0
H_γ	434.0	0.357	2469
H_δ	410.1	0.177	3812
H_ϵ	397.0	0.102	4617

APPENDIX 4

ESTIMATION OF THE MAXIMUM SPECIFIC ENTHALPY OF THE TOTAL MASS FLOW THROUGH THE CARBON-ARC REACTOR

The assumption was made that all the radiation lost from the mass was lost before the mass reached its maximum mean enthalpy, and that this was the only energy flow to be subtracted from the electrical power input to calculate the maximum mean enthalpy. The energy lost from the arc system by heat transfer down the electrodes may be thought to be an important loss, but it is assumed that all of this energy was returned to the arc chamber by convective heat transfer to the incoming hydrogen.

Measured values of radiation were used to establish the following estimates of the radiation loss from anode and arc.

Anode

At 20A, a radiation of 500W cm^{-2} of the anode surface was measured from the side (see chapter 6). It was assumed that 3800K blackbody radiation occurred at 50A - that is, 1200W cm^{-2}. For a surface area corresponding to 4 mm length of anode, the anode radiation amounted to 200W at 20A, and 500W at 50A. A linear interpolation was used between these currents.

Arc

At a current of 45A, a radiation of 8×10^{-3}W was measured through a solid angle of 6×10^{-4} sr <u>normal</u> to the chamber walls (chapter 6). To include radiation at an angle other than 90^{o} to the surface in the estimate, one would need to consider the extent of the arc within the arc chamber, and in particular the length

of arc which can be seen from any particular point on the arc wall for any angle from the normal. It appears from the photograph in the frontispiece that the arc extends perhaps to the walls at high currents, but the arc size is uncertain. Even if the geometric factors were known, an assumption of uniform intensity of radiation within each volume element of the arc would be needed to calculate a total radiation loss from the data obtained. However, since the radiation from the arc represents only 5% or less of the energy dissipated, a simple model will be used, which gives an upper limit on the arc radiation.

The chamber walls may be considered as a sphere of radius R/2 enclosing a spherical arc completely filling the sphere. The assumption of uniform intensity of radiation per unit volume is made. To obtain an upper limit, consider each surface element to be the centre of a hemisphere radiating to it with intensity I, given by $\frac{8 \times 10^{-3}}{6 \times 10^{-4} R^2}$ W $m^{-2} sr^{-1}$ where R = diameter of arc chamber in m.

For each element, the total radiation from the gas would then be π I W m^{-2}. For the total surface (area = $4\pi(R/2)^2 = \pi R^2$), the total radiation loss to the surface would then be $\pi R^2 \times 8 \times 10^{-3}/(6 \times 10^{-4} R^2) = \pi \times 8 \times 10^{-3}/6 \times 10^{-4} = 40$W from the arc. This radiated power was assumed proportional to the carbon ablation rate, for use with other currents.

Maximum Mean Specific Enthalpy

The maximum enthalpy was given the value

$(\mathring{e}_a - \mathring{q}_{r\ anode} - \mathring{q}_{r\ arc})/\mathring{m}$ kJ g^{-1}

where

$\dot{e}_a$ = power dissipated in the arc, kW

$\dot{q}_{r\ anode}$ = power radiated from anode, kW

$\dot{q}_{r\ arc}$ = " " " arc, kW

and $\dot{m}$ = total mass flow through the reactor.